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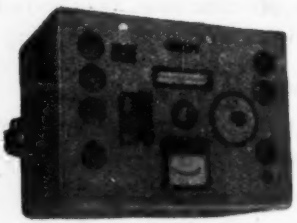

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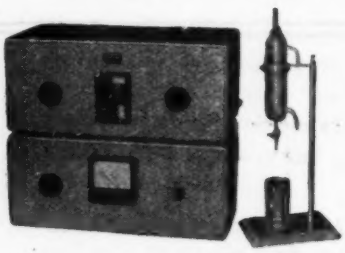

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[Jour. Indian Chem. Soc., Vol. 33, No 1, 1956]

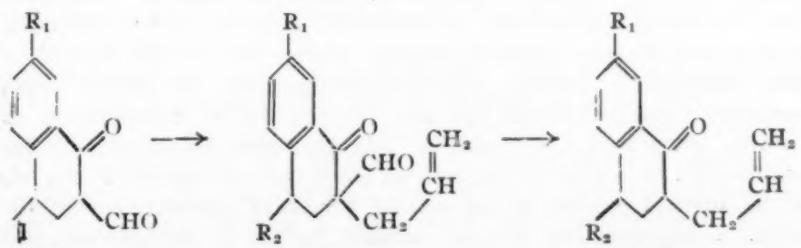
POLYNUCLEAR AROMATIC HYDROCARBONS. PART II. CONVENIENT SYNTHESIS OF SOME 3:4-BENZPHENANTHRENE DERIVATIVES

By V. S. Gaind, R. P. Gandhi, I. C. Lakhumna and S. M. Mukherji

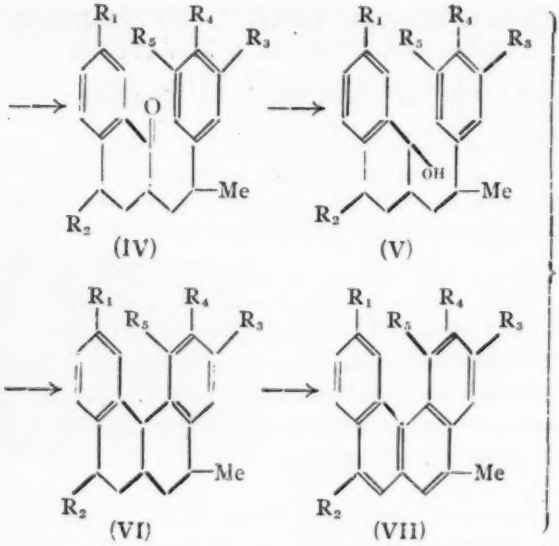
Several homologues of 3:4-benzphenanthrene, such as 2:9-dimethyl-, 2:9:3′-trimethyl- and 2:9:2′:4′-tetramethyl-3:4-benzphenanthrene have been synthesised by the application of the method developed by Mukherji *et al.* (*J. Org. Chem.*, 1954, **19**, 328). By following the same method, synthesis of 2-methyl-6-methoxy- and 2:3′-dimethyl-6-methoxy-3:4-benzphenanthrenes, as potential anti-carcinogens, has also been described.

In an earlier communication (Mukherji, Gaind and Rao, *J. Org. Chem.*, 1954, **19**, 328) we have described an elegant and convenient synthetic route to 3:4-benzphenanthrene derivatives. This method involves cationoid reaction between a benzene derivative and a γδ-unsaturated ketone, such as 2-allyl-1-tetralone system. To exploit this method further, it has now been extended to synthesis of a variety of homologues of 3:4-benzphenanthrene, following essentially the general conditions laid down by Mukherji *et al.* (*loc. cit.*).

The starting material, 4-methyl-1-tetralone, was prepared from ethyl allylacetate and benzene in 74% overall yield by the procedure prescribed by Mukherji, Vig, Singh and Bhattacharyya (*ibid.*, 1953, **18**, 1499). Formylation of this ketone, followed by allylation and decarbmonoxylation, furnished 2-allyl-4 methyl-1-tetralone (IIIa) in 54% overall yield. This unsaturated ketone was then condensed with benzene, toluene and *m*-xylene in presence of anhydrous aluminium chloride following exactly the condition of Mukherji, Gaind and Rao (*loc. cit.*), when the ketones (IV a, b and c) were obtained in 63%, 64% and 62% yield respectively. The orientation in the case of compounds from toluene (IVb) and *m*-xylene (IVc) was determined by their oxidative degradation with alkaline permanganate to mixtures of phthalic and terephthalic acids, and phthalic and trimesic acids respectively. No trace of *iso*phthalic acid in the former case and trimellitic acid in the latter could be detected, indicating that Friedel-Crafts' alkylation under our conditions gave exclusively a single isomer. This is supported by the fact that nowhere in the products of reactions to which the compounds (IVb and IVc) were subsequently subjected, could we get any indication of the presence of other possible isomers.



[a: R_1=H; R_2=Me. b: R_1=OMe; R_2=H]



a : $R_1 = R_3 = R_4 = R_5 = H$; $R_2 = Me$.

b : $R_1 = R_3 = R_5 = H$; $R_2 = R_4 = Me$.

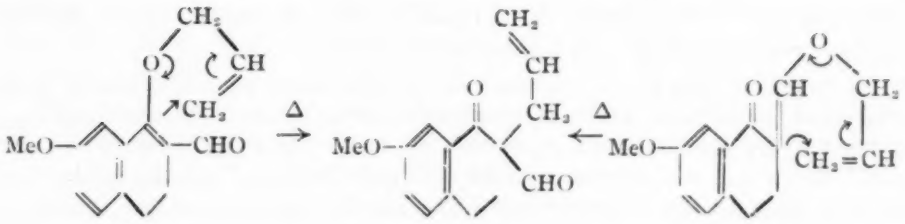
c : $R_1 = R_4 = H$; $R_2 = R_3 = R_5 = Me$.

d : $R_1 = OMe$; $R_2 = R_3 = R_4 = R_5 = H$.

e : $R_1 = OMe$; $R_2 = R_3 = R_5 = H$; $R_4 = Me$.

The ketones (IVa, b and c) were reduced by the Ponndorf method and the resulting carbinols (Va, b and c) cyclised with concentrated sulphuric acid at 0°. The final aromatic hydrocarbon derivatives (VIIa, b and c) were obtained by catalytic dehydrogenation of the cyclised products (VIa, b and c) over palladised charcoal (30%) (Linstead and Thomas, *J. Chem. Soc.*, 1940, 1130). These hydrocarbons were purified by regeneration from their picrates.

Our attention was then drawn to an observation by Cook and Schoental (*J. Chem. Soc.*, 1945, 288; 20th Annual Report of the British Empire Cancer Campaign, 1943, p. 20) that some monomethoxy derivatives of polycylic aromatic hydrocarbons strongly inhibited the growth of tumours. It was therefore thought of interest to synthesise some methoxy derivatives of 3 : 4-benzphenanthrene with varying degree of alkylation, and to test them for physiological properties. With this end in view we have synthesised 2-methyl-6-methoxy- and 2 : 3′-dimethyl-6-methoxy-3 : 4-benzphenanthrenes following essentially the same method as described above, the starting material being 7-methoxy-1-tetralone. Formylation of 7-methoxy-1-tetralone was effected according to the conditions of Mukherji, Gaind and Rao (*loc. cit.*). It is interesting to report that in earlier attempts at *C*-allylation of 2-formyl-7-methoxy-1-tetralone under the conditions described for 2-formyl-1-tetralone, we found that in contrast to the simple tetralone the allylated product in the case of 7-methoxy derivative was mainly the *O*-derivative. *C*-Allylation was, however, achieved by the Claisen rearrangement of the *O*-allyl derivative by its thermal treatment in presence of ammonium chloride as the catalyst.



(A) (II b) (B)

The *O*-allylated derivative is preferably represented as (A) instead of the alternative structure (B) involving enolisation of the formyl group, because on energetic grounds the former would be expected to be more stable. Furthermore, our preferential formulation (A) finds support in the generalisation postulated by Brown, Brewster and Shechter (*J. Amer. Chem. Soc.*, 1954, **76**, 467) that a reaction proceeds in such a manner as to favour the formation or retention of an exo double bond in the 5-membered rings and to avoid the formation or retention of the exo double bond in the 6-membered rings. However, this consideration would not affect the structure of the rearranged product (II b).

Hydrolysis of the *C*-allylated product furnished 2-allyl-7-methoxy-1-tetralone (III b) which was condensed with benzene and toluene in presence of anhydrous aluminium chloride. The orientation in the case of product (IV e) from toluene was proved, as earlier, by its oxidation with alkaline permanganate to a mixture of terephthalic and 4-methoxyphthalic acids. Terephthalic acid was identified as its dimethyl ester. No trace of *iso*phthalic acid could be detected, indicating the *para* orientation in the Friedel-Crafts alkylation step (cf. Mukherji, Gaind and Rao, *loc. cit.*).

The condensation products (IVd and IVe) were then reduced (Ponndorf), cyclised as above and dehydrogenated over palladium-charcoal (30%) when 2-methyl-6-methoxy- and 2 3′-dimethyl-6-methoxy-3:4-benzphenanthrenes were obtained in satisfactory overall yield. The aromatic hydrocarbon derivatives (VIId and VIIe) were purified through regeneration from their picrates. These compounds are now under biological testing.

EXPERIMENTAL *

4-Methyl-1-tetralone was prepared according to the procedure of Mukherji *et al.* (*loc. cit*, 1953).

2-Hydroxymethylene-4-methyl-1-tetralone (Ia).—Ethyl formate (9 4 g.) was added to cooled (ice-salt) suspension of dry sodium ethoxide (prepared from 3 g. sodium) in dry ether (250 c. c.) and the mixture left for 2 hours. 4-Methyl-1-tetralone (20 g.) was then added dropwise with shaking. After 6 hours the solid mass was poured onto crushed ice. The aqueous layer was separated and acidified when a red oil separated. This was taken up in ether which, after usual working up, furnished, on vacuum distillation, a light yellow oil (20 g., 80%) giving intense red coloration

* Melting and boiling points are uncorrected. Analyses are by Drs. Weiler and Strauss, Oxford.

with alcoholic ferric chloride, b. p. 145-46°/6 mm. (Found : C, 77.07 ; H, 6.00. $C_{12}H_{12}O_2$ requires C, 76.59 ; H, 6.38 per cent).

2-*Formyl*-2-*allyl*-4-*methyl*-1-*tetralone* (II a).—The above formyl compound (20 g.) was added dropwise to an ice-cold suspension of dry sodium ethoxide (from 2.5 g. sodium) in dry benzene (200 c. c.) and left overnight. Allyl iodide (18 g.) was then added slowly and the mixture refluxed for 8 hours when the supernatant layer gave negative ferric chloride coloration test. The reaction mixture was then decomposed with iced water and extracted with benzene. Vacuum distillation of the dried extracts, after solvent removal, yielded 18 g. (75%) of (IIa) as a yellow oil, b. p. 146°-150°/4 mm. (Found : C, 78.45; H, 6.72. $C_{15}H_{16}O_2$ requires C, 78.94 ; H, 7.01 per cent).

2-*Allyl*-4-*methyl*-1-*tetralone* (III a).—Hydrolysis of the above oil (10 g.) was effected by stirring with 150 c. c. of 5% NaOH solution at 50°-55° for 4 hours. The hydrolysed product was acidified, extracted with ether and dried over anhydrous sodium sulphate. After removal of the solvent the residue on distillation under reduced pressure furnished 7.8 g. (89%) of (III a), b. p. 140-42°/2 mm., η_D^{35}, 1.5372. (Found : C, 83.87 ; H, 7.79. $C_{14}H_{16}O$ requires C, 83.96 ; H, 8.05 per cent).

The 2 : 4-*dinitrophenylhydrazone*, prepared in the usual manner, was crystallised from ethyl acetate-alcohol as deep orange needles, m. p. 205°-206°. (Found : N, 15.20. $C_{20}H_{20}O_4N_4$ requires N, 14.73 per cent).

2-[*β-Methyl-β-(phenyl)-ethyl*]-4-*methyl*-1-*tetralone* (IV a).—Thiophene-free benzene (150 c. c.) was placed in a three-necked flask fitted with a mercury-sealed mechanical stirrer, a thermometer and a guard tube. Keeping the temperature at 0°-5°, anhydrous aluminium chloride (14.0 g.) and 2-allyl-4-methyl-1-tetralone (10 g.) were added alternately in four lots over a period of 40 minutes. Stirring was continued for 5 hours more when a deep red colour developed. The reaction mixture was decomposed with iced HCl and extracted with benzene. The extracts, after the usual working up, yielded 8.1 g. (63%) of (IV a), b. p. 208°-210°/2 mm. (Found : C, 86.06 ; H, 7.79. $C_{20}H_{22}O$ requires C, 86.28 ; H, 7.97 per cent).

2-[*β-Methyl-β-(phenyl)-ethyl*]-4-*methyl*-1-*tetralol* (V a).—The above ketone (6 g.) was reduced with Al-*iso*PrO from 2.5 g. of Al and 75 c. c. of *iso*propyl alcohol to obtain 5 g. (83%) of the corresponding carbinol at 196°-200°/2 mm., η_D^{35}, 1.5546. (Found : C, 85.48 ; H, 8.56. $C_{20}H_{24}O$ requires C, 85.66 ; H, 8.63 per cent).

2 : 9-*Dimethyl*-1 : 2 : 9 : 10 : 11 : 12-*hexahydro*-3 : 4-*benzphenanthrene* (VI a).—Cyclisation of the above carbinol (4 g.) was effected with 4 c. c. of H_2SO_4 (*d* 1.84) at ice-bath temperature. After three hours' standing the product was diluted with water and taken up in ether. After removal of the solvent the residue on distillation under reduced pressure furnished 3.2 g. (85%) of (VIa) at 205°-210°/2 mm., η_D^{35} 1.5646. (Found : C, 91.38 ; H, 8.40. $C_{20}H_{22}$ requires C, 91.55 ; H, 8.45 per cent).

2 : 9-*Dimethyl*-3 : 4-*benzphenanthrene* (VII a).—The hexahydro compound (1.5 g.) was dehydrogenated by heating for 4 hours with 30% palladium-charcoal (0.15 g.) at 300°-310°. A viscous mass was obtained on distillation under reduced pressure which readily furnished a dark red picrate. The picrate (1 g.) was decomposed with dilute ammonia to obtain the hydrocarbon (0.4 g.) which crystallised from benzene-

methanol mixture, m. p. 130° (lit. m. p. 130.6-31° ; Newman and Joshel, *J. Amer. Chem. Soc.*, 1934, **56**, 96). (Found : C, 93.90 ; H, 6.27. Calc. for $C_{20}H_{16}$: C, 93.71 ; H, 6.29 per cent).

The *picrate* of the above was prepared in the usual manner and crystallised from ethanol in dark red needles, m. p. 162° (lit. m. p. 164.6-65° ; *loc. cit.*). (Found : N, 8.60. Calc. for $C_{26}H_{19}O_7N_3$: N, 8.65 per cent).

2-[*β-Methyl-β-(p-tolyl)-ethyl*]-4-*methyl*-1-*tetralone* (IVb).—2-Allyl-4-methyl-1-tetralone (8 g.) was allowed to react with pure toluene (75 c.c.) in presence of anhydrous $AlCl_3$ under the same conditions as in (III a) when 7.5 g. (64%) of (III b) was obtained, b.p. 198°-202°/2 mm., η_D^{31}, 1.5582. (Found : C, 85.83 ; H, 8.04. $C_{21}H_{24}O$ requires C, 86.25 ; H, 8.27 per cent).

The above ketone (2 g.) was oxidised with quantitative amount of alkaline $KMnO_4$ solution (5%) when a mixture of phthalic and terephthalic acids was obtained. The latter, being insoluble in hot water, was separated and identified as its dimethyl ester, m. p. 140°, undepressed on admixture with an authentic sample of dimethyl terephthalate.

2-[*β-Methyl-β-(p-tolyl)-ethyl*]-4-*methyl*-1-*tetralol* (V b).—The above ketone (6 g.) was reduced with Al-*iso*PrO from 2.5 g. of aluminium foil in 75 c. c. of *iso*propyl alcohol. The usual working up of the product furnished 5 g. (83%) of the carbinol (V b), b. p. 206°-210°/3 mm., $\eta_D^{32\cdot6}$, 1.5544. (Found : C, 85.44 ; H, 8.84. $C_{21}H_{26}O$ requires C, 85.66 ; H, 8.90 per cent).

2 : 9 : 3′-*Trimethyl*-1 : 2 : 9 : 10 : 11 : 12-*hexahydro*-3 : 4-*benzphenanthrene* (VI b).—The carbinol (Vb ; 4 g.) was cyclised with H_2SO_4 (conc.) as in (VI a) and after the usual working up (VI b) was obtained in 82% yield, b.p. 200°-202°/3 mm., $\eta_D^{31\cdot6}$, 1.5734. (Found : C, 91.05 ; H, 8.67. $C_{21}H_{24}$ requires C, 91.30 ; H, 8.75 per cent).

2 : 9 : 3′-*Trimethyl*-3 : 4-*benzphenanthrene* (VII b).—The above hexahydro derivative (2 g.) was dehydrogenated with 30% palladium-charcoal (0.2 g.) at 300°-320° for 4 hours. The product after usual working up furnished 1.6 g. (81%) of a viscous oil which was purified by regeneration from its picrate and crystallised from alcohol-benzene mixture, m. p. 91°. (Found : C, 92.70 ; H, 6.63. $C_{21}H_{18}$ requires C, 91.29 ; H, 6.71 per cent). The *picrate*, prepared as above, was crystallised from alcohol, m p. 140°. (Found : N, 8.25. $C_{27}H_{21}O_7N_3$ requires N, 8.41 per cent).

2-[*β-Methyl-β-(m-xylyl)-ethyl*]-4-*methyl* - 1 - *tetralone* (IV c). — Pure *m*-xylene (70 c.c.) was allowed to react with 2-allyl-4-methyl-1-tetralone in presence of anhydrous $AlCl_3$ under the same conditions as in (IV a). The usual working up furnished 7.6 g. (62%) of (IV c), b.p. 218-22°/2 mm. (Found : C, 86.16 ; H, 8.28. $C_{22}H_{26}O$ requires C, 86.23 ; H, 8.55 per cent).

The above ketone was oxidised with alkaline $KMnO_4$ when a mixture of phthalic acid and trimesic acid was obtained, the latter being identified through its trimethyl ester, m. p. 143°. (Lit. m. p. 144°; Heilbron and Bunbury, "Dictionary of Organic Compounds", Vol. III, p. 847).

2-[*β-Methyl-β-(m-xylyl)-ethyl*] - 4 - *methyl* - 1 - *tetralol* (V c).—The Friedel-Crafts product (IVc ; 6 g.) was subjected to reduction with aluminium *iso*propoxide to obtain 4.8 g. (80%) of the tetralol, b.p. 210-12°/3 mm., $\eta_D^{34\cdot5}$, 1.5563. (Found : C, 85.42 ; H, 8.84. $C_{22}H_{28}O$ requires C, 85.66 ; H, 9.15 per cent).

2 : 9 : 2′ : 4′-*Tetramethyl*-1:2:9 : 10 : 11 : 12-*hexahydro*-3:4-*benzphenanthrene* (VI c).—Cyclisation of the above tetralol (4 g.) with H_2SO_4 (conc.) at 0° for 4 hours afforded on usual working up 3.2 g. (85%) of (VI c), b.p. 198°-200°/2 mm., η_D^{35}, 1.5738. (Found : C, 90.95 ; H, 8.67. $C_{22}H_{26}$ requires C, 90.98 ; H, 9.02 per cent).

2 : 9 : 2′ : 4′-*Tetramethyl*-3 : 4-*benzphenanthrene* (VII c).—The hexahydro product (2 g.) was dehydrogenated with 30% palladium-charcoal (0.2 g.) at 300°-310° for 4 hours. The product after usual working up furnished the hydrocarbon (1.8 g, 61%), b.p. 200°-205°/2 mm. Regeneration from its picrate did not furnish a solid hydrocarbon. (Found : C, 92.88 ; H 6.59. $C_{22}H_{20}$ requires C, 92.91 ; H, 7.09 per cent).

The *picrate* of the above hydrocarbon was crystallised from ethanol, m.p. 150°. (Found : N, 8.06. $C_{28}H_{23}O_7N_3$ requires N, 8.18 per cent).

2-*Hydroxymethylene*-7-*methoxy*-1-*tetralone* (I b).—7-Methoxy-1-tetralone (30 g.) was formylated, following the procedure adopted earlier, to obtain 26 g. (74%) of a light yellow mobile liquid, b.p. 170°-175°/5 mm. This gave an intense red coloration with alcoholic ferric chloride. (Found : C, 70.95 ; H, 5.72. $C_{12}H_{12}O_3$ requires C, 70.57 ; H, 5.92 per cent).

The *semicarbazone* of the above crystallised from dilute alcohol, m.p. 210°. (Found : N, 15.82. $C_{13}H_{15}O_3N_3$ requires N, 16.08 per cent).

2-*Formyl*-2-*allyl*-7-*methoxy*-1-*tetralone* (IIb).—The above formyl derivative (20.4 g.) was caused to react with allyl iodide under similar conditions as in (II a) to obtain 19.5 g. (80%) of *O*-allyl product. This was heated with ammonium chloride (5 g.) in an oil-bath at 180°-185° for 4 hours. After addition of water to dissolve the ammonium chloride, the oily product was extracted repeatedly with ether and the combined extracts dried over anhydrous sodium sulphate. After removing the solvent the residue on distillation under reduced pressure furnished 19 g. of (IIb), b.p. 195°-200°/5 mm. This gave no coloration with alcoholic ferric chloride. (Found : C, 73.68 ; H, 6.52. $C_{15}H_{16}O_3$ requires C, 73.75 ; H, 6.60 per cent).

2-*Allyl*-7-*methoxy*-1-*tetralone* (IIIb).—The above product (19 g.) on hydrolysis with 5% KOH (200 c.c.) at 50°-60° furnished 13.4 g. (79%) of the tetralone (IIIb) as a pale yellow oil, b.p. 165°-170°/5 mm., η_D^{28}, 1.5532. (Found : C, 77.58 ; H, 7.22. $C_{14}H_{16}O_2$ requires C, 77.77 ; H, 7.46 per cent).

2-[*β-Methyl-β-(phenyl)-ethyl*]-7-*methoxy*-1-*tetralone* (IVd).—2-Allyl-7-methoxy-1-tetralone (10.8 g.) was allowed to react with dry thiophene-free benzene in presence of anhydrous $AlCl_3$ under the conditions similar to (IVa) to obtain 9.0 g. (61%) of the tetralone (IV d), b. p. 220°-225°/4 mm., η_D^{28}, 1.5752. (Found : C, 82.02 ; H, 7.74. $C_{20}H_{22}O_2$ requires C, 81.60 ; H, 7.53 per cent).

The 2 : 4-*dinitrophenylhydrazone* was crystallised from ethyl acetate, m.p. 190°. (Found : N, 11.52. $C_{26}H_{26}O_5N_4$ requires N, 11.81 per cent).

2-[*β-Methyl-β-(phenyl)-ethyl*]-7-*methoxy*-1-*tetralol* (V d).—The above ketone (5 g.) was reduced with Al-*iso*PrO from 2 5 g. Al foil in 75 c.c. of *iso*propyl alcohol. After the usual working up, 4·2 g. (84%) of the corresponding carbinol distilled at 210°-215°/3 mm., $n_D^{34\cdot5}$, 1.5798. (Found : C, 81.40; H, 8.40. $C_{20}H_{24}O_2$ requires C, 81.04 ; H, 8.16 per cent).

2-*Methyl*-6-*methoxy*-1 : 2 : 9 : 10 : 11 : 12-*hexahydro*-3 : 4-*benzphenanthrene* (VI d).—Cyclisation of the above tetralol (3 g.) was effected with H_2SO_4 (conc., 3 c.c.), as described earlier. The cyclised product distilled at 210-12°/4 mm. as a gummy solid (2 g., 71%). (Found : C, 86 05 ; H, 7.83. $C_{20}H_{22}O$ requires C, 86.28; H, 7·97 per cent).

2-*Methyl*-6-*methoxy*-3 : 4-*benzphenanthrene* (VII d).—The above hexahydro compound (2 g.) was dehydrogenated with 30% palladium-charcoal (0.2 g.) for 4 hours at 300°-320°. On the usual working up, 1.4 g. (71%) of a viscous oil distilling at 210°-220°/4 mm. was obtained which readily furnished an orange picrate. The hydrocarbon was purified by regeneration from its picrate and crystallised from methyl alcohol in shining leaflets, m.p. 75°. (Found : C, 88.00 ; H, 5.86. $C_{20}H_{16}O$ requires C, 88.20 ; H, 5.92 per cent).

The above *picrate* was crystallised from ethyl alcohol, m.p. 119-20°. (Found : N, 8.31. $C_{26}H_{19}O_8N_3$ requires N, 8.38 per cent).

2-[*β-Methyl-β-(p-tolyl)-ethyl*]-7-*methoxy*-1-*tetralone* (IV e).—Reaction of 2-allyl-7-methyl-1-tetralone (10.5 g.) with pure toluene in the presence of anhydrous $AlCl_3$ under conditions similar to (IVa) furnished 9.5 g. (62%) of (IVe), b.p. 235°-240°/5 mm. (Found : C, 81.90 ; H, 7.58. $C_{21}H_{24}O_2$ requires C, 81.78 ; H, 7.84 per cent).

The above ketone (2 g.) was oxidised with alkaline $KMnO_4$ as earlier, when a mixture of terephthalic acid and 4-methoxyphthalic acid was obtained. The former was separated due to its greater insolubility in hot water and identified as its methyl ester, m.p. 142°, undepressed on admixture with an authentic sample of dimethyl terephthalate. 4-Methoxyphthalic acid melted at 162° (lit. m.p. 164° ; Fritsch, *Annalen*, 1897, **295**, 357).

2-[*β-Methyl-β-(p-tolyl)-ethyl*]-7-*methoxy*-1-*tetralol* (Ve).—The Ponndorf reduction of the above ketone (6 g.) was effected as in the earlier cases and the corresponding tetralol distilling at 230°-235°/5 mm. was obtained (4.8 g., 80%). (Found : C, 80.90 ; H, 8.20. $C_{21}H_{26}O_2$ requires C, 81.25 ; H, 8.44 per cent).

2:3'-*Dimethyl*-6-*methoxy*-1: 2: 9:10:11:12-*hexahydro*-3 : 4-*benzphenanthrene* (VIe).—The above carbinol (3 g.) was cyclised with 3 c.c. of sulphuric acid (conc.) in the usual manner to obtain 2 g. (72%) of the hexahydro compound, distilling at 225°-230°/5 mm. (Found : C, 85.81 ; H, 8.22. $C_{21}H_{24}O$ requires C, 86.25 ; H, 8.27 per cent).

2:3'-*Dimethyl-6-methoxy-3:4-benzphenanthrene* (VII e).—Dehydrogenation of the hexahydro compound (1 g.) with 30% palladium-charcoal gave, on usual working up, a viscous oil (0.7 g., 60%) distilling at 230°-235°/5 m m. This was converted into its picrate and the hydrocarbon regenerated therefrom was crystallised from methyl alcohol in shining plates, m.p. 79°. (Found : C, 87.80 ; H, 6.22. $C_{21}H_{18}O$ requires C, 88.08 ; H, 6.34 per cent).

Picrate of the above was crystallised from alcohol, m.p. 124°. (Found : N, 7.95. $C_{27}H_{21}O_8N_3$ requires N, 8.15 per cent).

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STUDIES IN COLLOIDAL ARSENIC TRISULPHIDE. PART I. DIALYSIS AND ELECTRICAL CONDUCTIVITY OF THE SOL

By A. K. M. Trivedi and M. J. Patani

On dialysis of colloidal arsenic trisulphide, the dialysate shows the presence of arsenious acid and sulphuric acid. The equivalent conductivity of the micelles does not show the behaviour of a typical colloidal electrolyte but is greater than that of the gegenion, if existing in a free condition.

Colloidal arsenic trisulphide sol has been the subject of numerous investigations (Weiser, "Inorganic Colloid Chemistry", Vol. III, 1938, pp. 167-221). Dialysis and conductivity of the sol were studied by many workers (Pauli and Semler, *Kolloid Z.*, 1924, **34**, 145; Desai and Barve, *Trans. Nat. Inst. Sci. India*, 1939, **2**, No. 2, 39; Murphy and Mathews, *J. Amer. Chem. Soc.*, 1923, **45**, 16 ; Rabinovitch and Dorfmann, *Z. physikal. Chem.*, 1928, **131**, 313 ; Mankodi *et al.*, *J. Univ. Bombay*, 1930, **5**, Pt. 2, 53 ; Joshi *et al.*, *Curr. Sci.*, 1934, **3**, 105 ; Jha and Ghosh, this *Journal*, 1945, **22**, 270). The properties of the sol have been interpreted with respect to hydrogen sulphide as a stabilising electrolyte.

In the case of aged arsenic trisulphide sol, on the other hand, Kargin and Klimovitzkaja (*J. Phys. Chem., U. S. S. R.*, 1934, **5**, 969) observed that arsenious acid rather than hydrogen sulphide was the stabilising electrolyte. Kharin (*Kolloid-Zhur*, 1948, **10**, 159) pointed out that aged arsenic trisulphide sols contained sulphuric acid in the intermicellar liquid. In the light of this information, the dialysis and the conductivity of the sol have been reinvestigated.

Experimental

Concentrated arsenic trisulphide sols were prepared by passing H_2S into a clear saturated solution of arsenious acid at room temperature till no free arsenious acid was present. The sols were concentrated by slow evaporation on a water-bath.

The sol was analysed as before for the colloid and arsenious acid contents (Trivedi and Patani, this *Journal*, 1952, **29**, 683) and sulphuric acid was determined as barium sulphate. The sol used for dialysis contained 60.1 g./litre of As_2S_3 and 33 and 2.1 m. e./litre of arsenious acid and sulphuric acid respectively.

The dialysis of colloidal arsenic trisulphide was carried out in a parchment paper bag, in cold, by adding sodium chloride as a reference substance. Chloride and arsenious acid contents in the dialysate were analysed from time to time. Initially, the dialysate was slightly yellow but contained very little arsenic trisulphide, which was neglected. After one or two changes of water, the dialysate was almost clear. The dialysis at higher temperatures was followed by analysing the dialysate for arsenious acid and sulphuric acid.

The conductivity of the sols was determined by using a Leeds and Northrup conductivity assembly. In the case of the two sols, A and B, conductivity was determined at different dilutions, the dilutions being performed after Trivedi, Divatia and Patani (*Proc. Ind. Acad. Sci.*, 1952, **36A**, 530). In measuring the conductivity of arsenic trisulphide sol, particularly on dilution, an interesting observation was made. There was a perceptible change of conductivity with time. This cannot be attributed to the liberation of the gegenions from the micelles as the change is fairly rapid. This phenomenon is unique in the sense that it has not been noticed in the case of sulphur sol (Bolam and Trivedi, *Trans. Faraday Soc.*, 1943, **39**, 247), iron oxide sol (Trivedi, Divatia and Patani, *loc. cit.*) and chromium oxide sol (Trivedi, Bhatt and Divatia, unpublished work). Hence, it was found necessary to take the readings as rapidly as possible.

Table I records the concentrations of the different constituents together with the data on conductivity of the sols under investigation.

TABLE I

Sol. No.	Colloid content (g./litre).	As_2O_3 (m.e./litre).	H_2SO_4 (m.e./litre).	Specific conductivity of the sol. ($K \times 10^3$).	Specific conductivity of H_2SO_4 ($K' \times 10^3$).	Specific conductivity of the micelles [$(K-K') \times 10^3$].
A	155.0	42	4.5	2.8	1.9	0.9
B	124.9	35	3.4	2.2	1.5	0.7
C	130.5	40	3.1	2.3	1.3	1.0
D	130.5	40	3.2	2.4	1.4	1.0

DISCUSSION

The results of dialysis in cold show that while the amount of chloride added as a reference substance is gradually reduced to a negligible proportion, the amount of arsenious acid remains practically constant. Arsenious acid is being continuously formed in the sol according to the equation

$$As_2S_3 + 3H_2O \longrightarrow As_2O_3 + 3H_2S.$$

This has been known for a long time (Weiser, *loc. cit.*). A part of hydrogen sulphide is converted into sulphuric acid, as first pointed out by Kharin (*loc. cit.*). Dialysis at a higher temperature has been found to increase the rates of formation of both As_2O_3 and H_2SO_4.

Arsenious acid is a very weak electrolyte, while sulphuric acid is a strong one. The formation of sulphuric acid throws light on the results of dialysis of the sol obtained by previous workers. Pauli and Semler (*loc. cit.*) dialysed the sol continuously and followed the changes on dialysis by measuring the conductivity of the sol from time to time, and found an initial sharp decrease in conductivity followed by a slow increase. As the work of Kharin (*loc. cit.*) as well as of ours shows, the sol investigated by Pauli might initially contain some sulphuric acid

depending upon the previous history of the sol, particularly whether it was kept in darkness or partly exposed to light. The initial sharp decrease in conductivity may be attributed to the removal of sulphuric acid by dialysis. The subsequent increase of conductivity suggests that the formation of sulphuric acid is more rapid than its removal on dialysis. Desai and Barve (*loc. cit.*) reported the decrease in conductivity, followed by an increase, and succeeded by a decrease. The first two points can be easily explained on the lines indicated above. The last one may be explained, following Desai and Barve, as due to "desorption of the primarily adsorbed ions". It is important to point out that both Pauli and Semler's experiments, as well as of Desai and Barve require that the rate of dialysis throughout must remain constant, a condition which is not easy to establish experimentally.

TABLE II

Sol A.			Sol B.		
Conc. of the sol.	$K \times 10^3$.	$(K/c) \times 10^5$.	Conc. of the sol.	$K \times 10^3$.	$(K/c) \times 10^5$.
100 %	2 8	2.8	100 %	2.2	2.2
90	2.6	2.9	75	1.7	2.3
80	2.3	2.9	50	1.1	2.2
70	2.0	2.9	25	0 58	2.3
60	1.7	2.8	10	0.25	2.5
50	1.4	2.8	5	0.13	2.6
40	1.1	2.8	2	0.06	3.0
30	0.85	2.9			
20	0.57	2.9			
10	0.30	3.0			

Table II records the values of the specific conductivity, K and K/c at different dilutions in the case of sols A and B. The original sols are taken as 100%. By analogy with sulphur, iron oxide and chromium oxide so's (*loc. cit.*) it was expected that the colloidal arsenic trisulphide might also exhibit the behaviour of a typical colloidal electrolyte, in the sense that the equivalent conductivity due to the micelles should decrease and then increase with dilution. The absence of this behaviour is probably connected with the formation of sulphuric acid which masks the actual variation of conductivity due to the micelles on dilution.

The results obtained become interesting when we consider the conductivity of the concentrated sols. The sols contain, besides the micelles, sulphuric acid and arsenious acid. The conductivity of arsenious acid is negligible (Zawidzki, *Ber.*, 1903, **36**, 1429). The specific conductivities of sulphuric acid solutions at various concentrations were read from a prepared graph of equivalent conductivity against concentration (c), the necessary data being obtained from the Handbook of Chemistry and Physics (Chemical Rubber Publishing Co., 29th Ed., 1945, pp. 1920, 1923). The specific conductivity due to the micelles is obtained by deducting the specific conductivity of sulphuric acid from that of the sol.

The data concerning the specific conductivity due to the micelles are shown in Table I. These values are subject to an error of about 10-20%. Taking the lowest

value of the specific conductivity due to the micelles and allowing for 20% error, the equivalent conductivity due to the micelles will be

$$\frac{1000 \times (0.7 \times 10^{-3}) \times 0.80}{0.035} = 16.0 \text{ ohms}^{-1} \text{ cm}^2.$$

The equivalent conductivity of free arsenious acid varies from 0.22/2 to 2.11/2 (Zawidzky, *loc. cit.*). Thus, the adsorbed arsenious acid appears to have a much greater equivalent conductivity than free arsenious acid. An alternative explanation would be, that the sol may contain an additional electrolyte, say polythionic acid. But polythionate was found absent, as further supported by Kharin (*loc. cit.*). The presence of any other electrolyte, besides sulphuric acid and arsenious acid, may be also ruled out by the data on ageing of arsenic trisulphide sol (Part II, this *issue*, p. 13).

Hence, one is left with a conclusion that when a weak electrolyte like arsenious acid is adsorbed by the colloidal As_2S_3, its conductivity, and therefore its dissociation, actually increases. Adsorption on a colloidal particle in the case of a weak electrolyte promotes ionisation.

The conclusion is rather surprising, but does not seem improbable (cf. Weiser, *loc. cit.*, Vol. II, 1938, p. 108). Jacques Gilbert's observation (*Compt. rend.*, 1952, **234**, 1916), that the conductivity due to the micelles in the case of arsenic trisulphide sol is considerably more than that can be accounted for by the conductivity of the original constituents or of the products of aerial oxidation, supports a similar view.

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STUDIES IN COLLOIDAL ARSENIC TRISULPHIDE. PART II. AGEING OF THE SOL

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Sunlight as well as oxygen is necessary for the ageing of arsenic trisulphide sol. When arsenic trisulphide sol is allowed to age, only arsenious acid and sulphuric acid are formed. The charge on the micelles decreases on ageing.

Sulphuric acid, even in the most favourable circumstances, can account for only a part of the hydrogen sulphide, which is formed on hydrolysis of arsenic trisulphide.

Arsenic trisulphide sols are fairly stable when kept in the dark. The authors have found a sample of concentrated arsenic trisulphide sol, kept in the dark for 4 years, not to suffer any apparent change, excepting deposition of a few particles in the bottom. The sol, kept in sunlight, on the other hand undergoes a quick change and ultimately coagulates. The effect of sunlight cannot be ascribed to the variation in temperature, as the sol can be boiled without any apparent significant change. The ageing of the sol in presence of light has been studied by a number of workers (Young and Pingree, *J. Phys. Chem.*, 1913, **17**, 657; Freundlich and Nathansohn, *Kolloid Z.*, 1921, **28**, 258; Dumanski, *ibid.*, 1925, **36**, 98; Murphy and Mathews, *J. Amer. Chem. Soc.*, 1923, **45**, 16; Joshi, Barve and Desai, *Curr. Sci.*, 1934, **3**, 105). The destabilising action of light and the increase in conductivity on ageing were ascribed to the formation of colloidal sulphur, stabilised by polythionic acid. Kharin (*Kolloid-Zhur*, 1948, **10**, 159), on the other hand, reports the absence of polythionic acid (hence of colloidal sulphur also) and attributes the destabilising action of light and the increase in acidity on ageing to the formation of sulphuric acid. In the present investigation, the absence of polythionic acid and the formation of sulphuric acid on ageing arsenic trisulphide sol have been confirmed by the study of the ageing of the sol, kept in the dark, and also by keeping it in sunlight for different intervals of time and in presence and absence of oxygen.

Experimental

Ageing of the sol was followed by analysing colloid, arsenious acid and sulphuric acid contents of the sol as well as by determining its conductivity under different conditions. Table I records the analysis of the different sols studied.

Table I

Sol No.	Colloid content.	Arsenious acid (m.e./litre).	Sulphuric acid (m.e./litre).
C	130.5 g./litre	40	3.1
D	130.5	40	3.2
E	128.0	40	3.1
F	73.4	27	1.0

Ageing in Sunlight

In these experiments about 300 ml. of the sol was kept in a 500 ml. conical flask and tightly corked. The sols were exposed to direct sunlight for about 4 hours a day and for the remaining time they were exposed to day light. The sols were kept for a total of about 100 hours in sunlight. The ageing of the sol was followed by measuring at intervals the conductivity as well as the concentrations of As_2O_3 and H_2SO_4. Two sets of experiments were performed (Table II).

TABLE II

	Sol C.				Sol D.			
	Time.	Sp. condy. ($K \times 10^3$).	As_2O_3 conc. (m.e./litre).	H_2SO_4 conc. (m.e./litre).	Time.	Sp. condy. ($K \times 10^3$).	As_2O_3 conc. m.e./litre).	H_2SO_4 conc. (m.e./litre).
1	0 hr.	2.3	40	3.1	0 hr.	2.4	40	3.2
2	30	4.0	57	8.0	20	4.6	61	9.1
3	65	5.6	79	13.0	70	4.9	76	11.7
4	85	6.8	100	17.5	100	6.7	102	17.6

Ageing on Dilution

In this series of experiments, the sol was kept (*i*) in darkness, (*ii*) in sunlight for 70 hours and (*iii*) in sunlight for 95 hours. The sols in three different dilutions were placed in Pyrex test tubes and tightly corked. As before, the concentrations of As_2O_3 and H_2SO_4 were also determined (Table III).

TABLE III

Sol E.

Expt.	Sol content	Arsenious acid (m.e./litre).			Sulphuric acid (m.e./litre).		
		I.	II.	III.	I.	II.	III.
1	100.0%	40	57	...	3.1	8.1	...
2	50.0	21	45	65	1.7	7.6	16.5*
3	25.0	12	40	42	1.1	7.4	10.4
4	12.5	7	22	61	0.6	5.8	15.9*

I—In the dark for 40 days.
II—In sunlight for 70 hours.
III—In sunlight for 95 hours.
* At the time of the analysis, the sols were on the verge of coagulation.

Ageing in Sunlight on passing Hydrogen and Oxygen

According to Krestinskaya and Yakovleva (*Kolloid Z.*, 1933, **65**, 187), oxygen is necessary for the ageing of the sol. This was tested as follows. Oxygen from oxygen cylinder or hydrogen from Kipp's, purified through $KMnO_4$ solution, was bubbled through the sol, kept in a wash-bottle for five hours in sunlight. No attempt was made to measure the rate of passing the gases. The contents of arsenious and sulphuric acids are shown in Table IV.

TABLE IV

Sol F.

Expt.	Duration of passing the gas.	Oxygen. As_2O_3 (m.e./litre).	Oxygen. H_2SO_4 (m.e./litre).	Hydrogen. As_2O_3 (m.e./litre).	Hydrogen. H_2SO_4 (m.e./litre).
1	5 hrs	127	17.2	34	1.1
2	5	119	14.9	33	1.1
3	5	121	15.4	33	1.1
4	5	127	17.7	35	1.2

DISCUSSION

It appears from Table III that when the sol is kept in darkness, practically no ageing takes place even on dilution, and when it is kept in sunlight, ageing is promoted to an extent depending directly upon the duration of exposure to sunlight. When it is diluted to different extents, the formation of both arsenious as well sulphuric acid is promoted ; the rate of formation of sulphuric acis also appears to be much greater than that of arsenious acid. Thus, when the sol was diluted eight times and kept in sunlight for seventy hours, the formation of arsenious acid increased three times, while the formation of sulphuric acid increased nearly eight times. Hence, one may conclude that sunlight promotes ageing, particularly the formation of sulphuric acid. Dilution accelerates the effect of ageing.

The effect of oxygen and hydrogen can be seen from the data in Table IV. In the absence of oxygen practically no ageing takes place. Oxygen promotes ageing. Here again sulphuric acid is formed to a much greater extent than arsenious acid.

TABLE V

Expt.	(*i*) Sol C. Time.	Specific conductance of Sol ($K\times10^3$).	H_2SO_4 ($K'\times10^3$).	Micelles. $[(K-K')\times10^3]$.	(*ii*) Sol D. Time.	Specific conductance of Sol. ($K\times10^3$).	H_2SO_4 ($K'\times13^3$).	Micelles $[(K-K')\times10^3]$.
1	0 hr.	2.3	1.3	1.0	0 hr.	2.4	1.4	1.0
2	30	4.0	3.2	0.8	20	4.6	3.6	1.0
3	65	5.6	4.9	0.7	70	4.9	4.5	0.4
4	85	6.8	6.4	0.4	100	6.7	6.5	0.2

Table V shows the data on the specific conductivities of the sol, of sulphuric acid and of that due to the micelles (vide Part I, this *issue*, p. 9). The conductivity of arsenious acid is very low (Zawidzki, *Ber.*, 1903, **36**, 1429) and hence, it is not taken into account. It is obvious that in both the sets of experiments, although the specific conductivity of the sol increases, that due to the micelles decreases. This shows that the residual conductivity is due to the micelles only. The decrease of charge on ageing is a normal feature of the colloidal system (see for example, Joshi, Barve and Desai, *loc. cit.*). The importance of the data lies particularly in the fact that *the sol on*

ageing forms sulphuric acid and arsenious acid and no other electrolyte. For, if any other electrolyte were formed, the residual conductivity, reported in the last column, could not have decreased as it actually has done. The significance of this observation is with regard to the calculations of the equivalent conductivity due to the micelles (vide Part I, *loc. cit.*).

We may now consider the relation between the arsenious acid (*a*) and the sulphuric acid (*b*) formed on ageing under different conditions.

TABLE VI

No.	Rate a/b.	Remarks.
1	28	In presence of hydrogen and sunlight for five hours (Table IV).
2	31	
3	29	
4	29	
5	13	In dark for 40 days [Table III (I)].
6	12	
7	11	
8	12	
9	7	In presence of oxygen and sunlight for five hours (Table IV).
10	8	
11	8	
12	7	
13	13	In sunlight for different periods (Table II).
14	7	
15	6	
16	6	
17	14	Do
18	7	
19	7	
20	6	
21	7	In sunlight for 70 hours; sols diluted to different extents [Table III (II)].
22	6	
23	5	
24	4	
25	4	In sunlight for 95 hours; sols diluted to different extents [Table III (III)].
26	4	
27	4	

Three moles of sulphuric acid per mole of arsenious acid should be formed, provided that all the hydrogen sulphide formed on hydrolysis of the sol is converted into sulphuric acid (vide Part I, *loc. cit.*). The data in Table VI show that even in the most favourable circumstances, formation of sulphuric acid can account for only a part of hydrogen sulphide. The fate of the remaining hydrogen sulphide awaits further experimental data, since either free sulphur or colloidal sulphur, stabilised by polythionic acid, appears to be absent.

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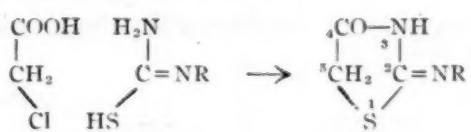
PREPARATION OF 4-THIAZOLIDONES AND THEIR 5-(*p*)-SULPHONAMIDOPHENYLAZO DERIVATIVES

By G. N. Mohapatra and M. K. Rout

Fifteen different 2-arylimino-4-thiazolidones have been synthesised by two different methods, and the yields obtained by both the methods have been compared. The resulting thiazoalidone compounds have been coupled with diazotised sulphanilamide giving rise to fifteen different 5-sulphonamidophenylazo derivatives. Experimental evidence has been adduced to support the observation that the azo group is linked to the CH_2 group in 5-position of the thiazolidone nucleus.

In view of the close relationship between thiazole and thiazolidones and the reported use of thiazolidone compounds as anaesthetics (Surrey, *J. Amer. Chem. Soc.*, 1949, **71**, 3354), anticonvulsants (Troutman and Long, *ibid.*, 1948, **70**, 3436) and amoebacidal agents (Surrey and Cutler, *ibid.*, 1954, **76**, 578), it was considered worthwhile to carry out investigations for preparing new types of 4-thiazolidone derivatives and explore new directions of applications of the resulting compounds.

Thiazolidone compounds have been synthesised by various methods (Surrey, *ibid.*, 1947, **69**, 2911 ; Ratnar and Clarke, *ibid.*, 1937, **59**, 200 ; Mathes and Stewart, *ibid.*, 1950, **72**, 1879). In the present investigation fifteen different 2-arylimino-4-thiazolidones have been prepared by two methods, and the yields obtained in both the methods have been compared. In the first method, already reported (Das and Rout, this *Journal*, 1954, **31**, 617), aryl-substituted thioureas were condensed with monochloroacetic acid in alcohol in presence of anhydrous sodium acetate. The reaction proceeds according to the following scheme, leading to a product of the following structure.



(I)

Reasons for assigning the thiazolidone structure to the above compounds have already been reported (Das and Rout, *loc. cit.*).

The second method adopted involves condensation of ethyl monochloroacetate with arylthioureas in absolute alcohol using sodium ethoxide as the condensing agent. The yields obtained in each case by both the methods have been compared and are recorded in Table I.

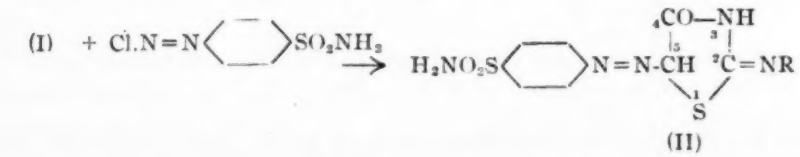
Both the experimental procedures are illustrated in the experimental in the preparation of 2-phenylimino-4-thiazolidone.

The thiazolidone compounds prepared above have been coupled with diazotised sulphanilamide. It has been assumed that the azo group is attached to the thiazolidone nucleus in position-5 ; the assumption is based on the following evidences. Bogert and Cherbcoff (*J. Amer. Chem. Soc.*, 1924, **46**, 2864 ; *Proc. Nat. Acad. Sci.*, 1924, **10**, 418) obtained dyes by coupling diazotised *p*-nitroaniline and sulphanilic acid with 2-aminothiazole in which they observed that the azo group was attached to position-5 of the thiazole nucleus. Ganapathi and Venkataraman (*Proc. Ind. Acad. Sci.*, 1945, **22A**, 348) and Beyer and Wolter (*Chem. Ber.*, 1952, **85**, 1077) confirmed the above observations ; the former workers used this reaction for the preparation of 5-amino-2-hydroxythiazoles. On account of a close resemblance between thiazole and thiazolidones, the same behaviour is also expected of thiazolidones.

Meerwein, Buchner and Engster (*J. prakt. Chem.*, 1939, **152**, 237) after a detailed study of the reactions of diazonium salts with $\alpha\beta$-unsaturated carbonyl compounds concluded that the arylazo group entered the position α to the activating group. This is also supported by the work of Kvalnes (*J. Amer. Chem. Soc.*, 1934, **56**, 2478) and Freund (*J. Chem. Soc.*, 1951, 1943), who made use of this reaction in preparing 2-aryl-1 : 4-benzoquinones and 3-*p*-arsonophenylcoumarin. In thiazolidones, the CH_2 group in position-5 is in α-position to the activating carbonyl group ; hence, the placement of the azo group in position-5 is justified. Zeigler has also made similar observations in case of pyrazolones and formulated the structure of the yellow dye, Tartrazine, accordingly.

This conclusion gains further support from the fact that when the CH_2 group in position-5 of the thiazolido nenucleus is blocked by condensation with aromatic aldehyde or by substitution of the hydrogen atoms by alkyl groups, which could be easily achieved by replacing chloroacetic acid or ester by α-bromo*iso*butyric acid or ester in the synthesis of thiazolidone compound, no azo dye is formed.

The azo dye formed by coupling of diazotised sulphanilamide with 2-phenylimino-4-thiazolidone has also been found to be inert towards condensation with aromatic aldehydes. This conclusively proves that the coupling takes place in position-5, *i.e.* at the CH_2 group, as shown below :



(II)

EXPERIMENTAL

Preparation of Arylthioureas.—The phenyl- and *o*-, *m*- and *p*-tolylthioureas were prepared by the action of alcoholic NH_3 on the corresponding *iso*thiocyanates obtained by the methods of Dains and others ("Organic Synthesis", Vol. I, p. 437). The *o*-, *m*- and *p*-(chloro-, carboxy- and nitro)-phenyl- and α- and β-naphthyl- thioureas were obtained by the action of ammonium thiocyanate on the hydrochlorides of the compounding bases (De Clermont, *J. Chem. Soc.*, 1877, **31**, 7).

Preparation of 2-Phenylimino-4-thiazolidone: *Method* I.—Phenylthiourea (5 g.) was heated under reflux with monochloroacetic acid (4 g.) in presence of anhydrous sodium acetate (3 g.) and absolute alcohol (25 c.c.) on a water-bath for 3 to 4 hours. The reaction mixture was poured into water when a precipitate was formed. The precipitate was washed several times with boiling water and finally recrystallised from alcohol, yield 6 g., m.p. 175°. (Found: C, 56.65; H, 4.81; N, 13.89; S, 16.99. $C_9H_8ON_2S$ requires C, 56.25; H, 4.16; N, 14.58; S, 16.66 per cent).

Method II.—Phenylthiourea (6 g.) was heated under reflux with ethyl chloroacetate (4.8 g.) in presence of sodium ethoxide (5 g.) and 25 c.c. of absolute alcohol on a water-bath for 2 to 3 hours. The reaction mixture was poured into water and acidified with acetic acid when a precipitate was formed. The precipitate was washed several times with boiling water and finally recrystallised from alcohol, m. p. 175°, yield 7.3 g. (Found: C, 55.78; H, 4.29; N, 14.31; S, 16.13. $C_9H_8ON_2S$ requires C, 56.25; H, 4.16; N, 14.58; S, 16.66 per cent).

Preparation of 5-(p)-sulphonamidophenylazo-2-phenylimino-4-thiazolidone.—Sulphanilamide (1 g.), dissolved in glacial acetic acid (2 c.c.) and water (100 c.c.), was diazotised with $NaNO_2$ (0.5 g. in 30 c. c. of water) in an ice-bath. The resulting diazo solution was added gradually with stirring to a previously well cooled solution of 2-phenylimino-4-thiazolidone (1 g.) in dilute NaOH solution (1 g. in 40 c.c. of water), kept in an ice-bath. After addition the reaction mixture was stirred for another hour. The orange-coloured dye separated out and was collected and recrystallised from alcohol, m.p. 85°, yield 1.5 g. (Found: C, 48.0; H, 3.47; N, 18.66; S, 17.06. $C_{15}H_{13}O_3N_5S_2$ requires C, 47.25; H, 3.53; N, 17.95; S, 16.92 per cent).

TABLE I

2-Arylimino-4-thiazolidone (I).

Compound No.	Nature of aryl group R.	M. P.*	Yield by method I.	Yield by method II	% Nitrogen. Found.	% Nitrogen. Calc.	% Sulphur. Found.	% Sulphur. Calc.
1	Phenyl	175°	90%	95%	14.41	14.58	16.13	16.66
2	*o*-Tolyl	136°	85	87	13.87	13.59	14.97	15.53
3	*m*- ,,	160°	80	82	13.14	13.59	15.19	15.53
4	*p*- ,,	191°	75	82	12.79	13.59	15.65	15.53
5	*o*-Nitrophenyl	147°	50	60	...	...	13.32	13.50
6	*m*- ,,	210°	52	55	...	...	12.91	13.50
7	*p*- ,,	235°	55	60	...	...	12.83	13.50
8	*o*-Chlorophenyl	144°	65	70	11.58	12.31	14.01	14.13
9	*m*- ,,	181°	68	70	11.79	12.31	14.73	14.13
10	*p*- ,,	200°	70	75	11.98	12.31	13.97	14.13
11	*o*-Carboxyphenyl	190°	50	55	11.05	11.86	13.13	13.56
12	*m*- ,,	255°	53	55	12.06	11.86	13.86	13.56
13	*p*- ,,	>360°	51	56	10.58	11.86	12.77	13.56
14	α-Naphthyl	184°	90	95	11.07	11.57	13.52	13.22
15	β- ,,	220°	92	95	10.91	11.57	12.83	13.22

TABLE II

2-Arylimino-5-sulphonamidophenylazo-4-thiazolidones (II).

Compound No. **	Colour.	* M.P.	Yield.	% Nitrogen.		% Sulphur.	
				Found.	Calc.	Found.	Calc.
1	Orange	85°	50%	17 95	18.66	16.92	17.06
2	Deep yellow	102°	55	16.98	17.99	15 97	16.45
3	Brown	>350°	58	17.53	17.99	15.72	16.45
4	Brown	285°	60	17.29	17.99	15.83	16.45
5	Dirty brown	70°	65	...	...	15.72	15.24
6	Yellow	112°	61	...	...	15.12	15.24
7	Brown	78°	56	...	...	14.89	15.24
8	Yellowish brown	118°	65	16.81	17.09	15.19	15.63
9	Yellow	195°	70	16.37	17.09	14.77	15.63
10	Orange	150°	71	17.51	17.09	15.83	15.63
11	Yellow	>350°	50	16.21	16.70	14.98	15.27
12	Yellowish brown	>350°	52	15.92	16.70	15.63	15.27
13	Yellowish brown	>350°	56	16.81	16.70	15.19	15.27
14	Chocolate-red	105°	70	16 19	16.47	14.39	15.06
15	Orange-red	136°	78	16.05	16.47	14.81	15.06

* All the melting points have been taken on Gallencamp's electrically heated melting point apparatus.

** The nature of aryl group R corresponding to those in Table I.

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SALICYLAMIDOXIME AS AN ANALYTICAL REAGENT. PART I. REACTIONS OF SALICYLAMIDOXIME WITH METALLIC IONS

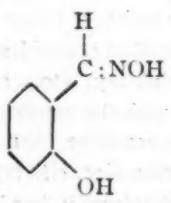
By Debabrata Bandyopadhayay and Privadaranjan Rây

The reactions of salicylamidoxime with various metallic ions have been fully investigated. It has been found that this substance behaves very much like the aldoxime with respect to the colour, solubility, etc. of its metallic derivatives; but the p_H of incipient precipitations of the metallic ions are somewhat higher in case of the amidoxime. Both these substances have been found to produce orange-yellow precipitates with titanium^{IV} in acid solution, although Flagg and Furman failed to observe any such reaction in their investigation on salicylaldoxime.

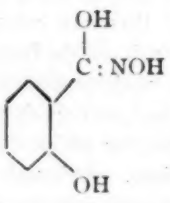
Copper (light green), nickel (greyish violet) and palladium (light yellow) compounds after drying at 110° have got the composition $(C_7H_7O_2N_2)_2M$ (where M = Cu, Ni, Pd). The nickel and palladium compounds have been found to be diamagnetic, as is to be expected for dsp^2 square-planar complexes of these bivalent metals. The copper compound is paramagnetic ($\mu_B = 1.81$).

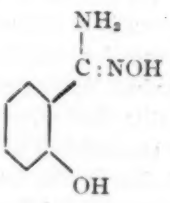
The identification limits for Cu, Ni and Bi by precipitation and that of Fe^{III} and U^{VI} by the formation of soluble colours in alkaline solution have been determined. Ti^{IV} and V^{V} afford coloured precipitates in acid solution, which are soluble in *iso*amyl alcohol. This has been made use of in the detection of these metals.

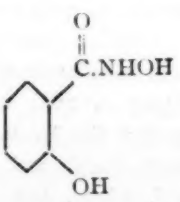
The reactions of *o*-hydroxybenzamidoxime or salicylamidoxime with various metallic ions have been fully investigated in an effort to find the possibility of using this substance as an analytical reagent. This substance, as also the compound salicylhydroxamic acid, contains the same copper specific group of *o*-hydroxy-arylaldoximes, e.g., salicylaldoxime, as will be evident from the following representations of the three substances:



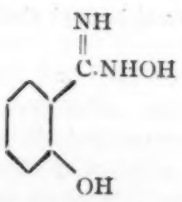
(Salicylaldoxime)







(Salicylhydroxamic acid)



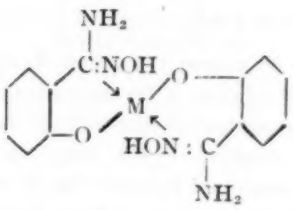
(Salicylamidoxime)

Salicylaldoxime was first employed by Ephraim (*Ber.*, 1930, **63**, 1928 ; 1931, **64**, 1210, 1215) for the detection and gravimetric determination of copper. Later on Flagg and Furman (*Ind. Eng. Chem. Anal. Ed.*, 1940, **12**, 529) studied the reactions of this substance, as also of its 5-chloro, 3 : 5-dibromo and 5-nitro derivatives, with various metallic ions. Since then several reports have appeared on the use of salicylaldoxime for the separation and determination of metals (Welcher, "Organic Analytical Reagents", Vol. III, pp. 259-71, D. Van Nostrand Co., Inc., 1947).

In recent years several reports have also appeared on the analytical reactions and applications of salicylhydroxamic acid (Musante, *Gazzetta*, 1948, **78**, 536 ; Bhaduri and Rây, *Science & Culture*, 1952, **18**, 95). It might therefore be interesting to investigate the reactions of salicylamidoxime as well, which is related to the two compounds referred to above. The results of such an investigation will naturally show the influence of a substituent $-NH_2$ group in place of the hydrogen atom, in the open-chain carbon atom of the aldoxime or of a corresponding -OH group in salicylhydroxamic acid. Incidentally, it might be pointed out that the -OH and $-NH_2$ groups are isoelectronic, but the former is acidic while the latter is basic in character in the particular cases concerned. Hence, a comparison of the reactions of the two substances might be suggestive of the influence of a basic constituent in place of an acidic one of the same electronic configuration. Furthermore, salicylamidoxime might be expected to offer some practical advantage over the aldoxime or the hydroxamic acid as a reagent, particularly because of its greater stability compared to that of the aldoxime and its solubility in acids and alkalies in which the reagent solution can be prepared (cf. Spilker, *Ber.*, 1889, **22**, 2773 ; vide, properties of salicylamidoxime in the "Experimental").

An account of the general reactions of salicylamidoxime with various metallic ions is given in a following section. If these are compared with the results of Flagg and Furman (*loc. cit.*) for salicylaldoxime, it will be found that the amidoxime resembles the aldoxime, in its general behaviour, with respect to the colour, solubility, etc., of its metallic derivatives, but the p_Hs of incipient precipitation of metals with the amidoxime are somewhat higher. Furthermore, the amidoxime is much less sensitive than the aldoxime for the detection of vanadium. Although Flagg and Furman (*loc. cit.*) report that salicylaldoxime does not give any positive reaction with titanium, it has been found, however, that both the amidoxime and the aldoxime produce orange-yellow precipitates with Ti^{IV} in acid solution, which are soluble in organic solvents like chloroform and *iso*amyl alcohol.

Cu^{II}, Ni^{II} and Pd^{II} compounds of salicylamidoxime were prepared as usual by precipitation ; after washing and drying at 110° their compositions were found to correspond to $(C_7H_7O_2N_2)_2$ M (where M = Cu, Ni, Pd). From the known constitution of the metal-salicylaldoxime compounds (Feigl and Bondi, *Ber.*, 1931, **64**, 2819 ; Cox, Pinkard, Wardlaw and Webster, *J. Chem. Soc.*, 1935, 459, 1475), the metal-salicylamidoximes may be represented by the following structure :



[M = Cu, Ni, Pd]

The solubility of these compounds in strong alkali solutions may be due to salt formation by the :NOH group, whereby the non-electrolytic complexes are converted into complex anions (cf. Feigl and Suter, *J. Chem. Soc.*, 1948, 378 ; Thilo and Friedrich, *Ber.*, 1929, **62**, 2998).

The nickel and palladium compounds have been found to be diamagnetic, which supports a square-planar structure of the dsp^2 bond-type. The copper compound is paramagnetic as usual.

Precipitation of copper, nickel, titanium and bismuth from aqueous solution by excess of salicylamidoxime affords a convenient method of detecting these metals. The identification limits, which are rather low, have been determined.

U^{VI} and Fe^{III} produce yellow and orange-red colour respectively with excess of the amidoxime in alkaline solution. Ti^{IV} and V^{V} produce orange-yellow and black precipitates respectively in acid solution, which can be extracted into *iso*amyl alcohol producing yellow and pink coloured layers. These have been made use of for the colorimetric detection (visual) of these metals.

Experimental

Salicylamidoxime (cf. Spilker, *loc. cit.*) was prepared by heating together salicylnitrile, hydroxylamine hydrochloride and Na_2CO_3 in aqueous-alcoholic solution for 4 to 5 hours at 90° in a pressure bottle. The mixture was then acidified with HCl and most of the alcohol distilled off on the water-bath. The residue was then cooled and treated with HCl to 1 *N* and repeatedly extracted with ether to remove the impurities. From the aqueous solution the amidoxime was precipitated by adding sodium bicarbonate. This was then recovered by extracting with ether and removing the ether in vacuo. The product was purified by crystallisation from hot water, after decolorising with active charcoal, and finally by dissolving in hot benzene and precipitating it with petroleum ether (boiling range 40°-60°). The pure product gave fine white needle-shaped crystals, m. p. 97-98°.

The substance is easily soluble in alcohol, ether, chloroform, benzene, etc., but is insoluble in petroleum ether. It is only slightly soluble in cold water, but is more or less easily soluble in hot water. Dilute solutions of mineral acids and alkalies dissolve it readily. In aqueous or dilute hydrochloric acid solutions it remains unchanged even on boiling. The solid after melting remains unchanged even at 125°.

p_H-limits for the Precipitation of Metals

A fairly concentrated (1 *N* approx.) solution of alkali (NaOH) was added with stirring to 200 c.c. of a 0.001*M* solution of the metal-ion containing sufficient free acid and about 20% excess of the equivalent quantity of salicylamidoxime till a turbidity just appeared. The p_H of the solution at this point was determined with the help of a p_H-meter (Cambridge, bench type) and this gave the p_H of incipient precipitation of the metal-ion under the prescribed conditions. From this point onward the addition of alkali was continued and the p_H of the filtered solution was ascertained at intervals, and the metal-ion was tested for in the filtrates. The p_H just corresponding to the complete precipitation was thus obtained. These p_H-limits are recorded along with the general reactions of the amidoxime in Table I.

TABLE I

Reactions of salicylamidoxime with metallic ions.

Metal-ion.	Nature of reaction.	p_H of incipient pptn. in 0.001*M* soln. of metallic ion.	Remarks.
Ag^+	Light yellow precipitate in neutral soln.	...	Precipitate soluble in acids and ammonia; solution in latter deposits silver as a mirror. Caustic alkalies convert the precipitate immediately into black metallic silver.
Pb^{2+}	White ppt.	6.6	Precipitate soluble in caustic soda.
Hg^{2+}	Light yellow ppt.	6.4	Precipitate decomposed by ammonia.
Cu^{2+}	Light green ppt.	3.2	Precipitate is soluble in ammonia and caustic soda. Precipitation is complete at and above p_H 3.9 (at least up to 6.5 p_H) in 0.001 *M* soln. of copper ion. Precipitate slightly soluble in solutions of alkali acetates, tartrates, ammonium chloride, but precipitation complete even in their presence if excess of reagent is used. It is completely insoluble in hot water and not decomposed by it.
Cd^{2+}	White crystalline ppt.	8.2	Precipitate is soluble in ammonia, and no precipitation occurs in presence of NH_4Cl.
Bi^{3+}	Yellow ppt. in caustic alkali soln.	p_H 9 approx.	Precipitate is stable to excess of NaOH.
Zn^{2+}	White crystalline ppt. in alkaline soln.	7.2	It is soluble in NaOH and also in NH_4OH; NH_4Cl prevents precipitation.

TABLE I (*contd.*)

Metal-ion.	Nature of reaction.	p_H of incipient pptn in 0.001 *M* soln of metallic ion.	Remarks.
Mn^{2+}	Dirty green ppt. in alkaline medium.	8.7	A greenish colour first appears at 7.2 p_H. Precipitate is soluble in NaOH and also in NH_4OH. Precipitation occurs even in presence of NH_4Cl; the addition of H_2O_2-NH_4OH causes instantaneous precipitation.
Co^{2+}	Brown ppt. even in presence of NH_4Cl.	6.9	It is soluble in NH_4OH and in NaOH solutions.
Ni^{2+}	Light green ppt. in the cold and greyish violet in warm soln.	5.6	The colour of the green precipitate changes to greyish violet slowly on standing, but rapidly on warming. Precipitation is complete at and above p_H 6.7 in 0.001*M* solution of nickel ion, and at least up to p_H 8. It is soluble in aqueous solutions of ammonia and of NH_4Cl. Even in presence of NH_4Cl complete precipitation occurs if the reagent be in excess.
Pd^{2+}	Yellow ppt. in acid soln. in presence of NaCl.	1.0 (approx.)	Precipitate is soluble in ammonia and NaOH solutions.
Fe^{2+}	In presence of a reducing agent like NH_2OH, HCl or H_2SO_3, to prevent aerial oxidation, a brown ppt. is obtained.	5.5-6.0	It is soluble in NaOH and ammonia solutions forming red colour.
Fe^{3+}	Red-violet colour at 3.5-4.0 p_H and orange-red above p_H 6.	...	Light orange colour persists even up to 11 p_H. In concentrated solutions of Fe^{3+} ion a red-brown precipitate appears at 5.5-6.0 p_H which dissolves in NaOH giving an orange-red solution. Colour is bleached by F^-, PO_4^{3-} and $C_2O_4^{2-}$ ions. The soluble coloured products cannot be extracted into organic solvents, although the precipitate is soluble in *iso*amyl alcohol giving a dark red solution.
UO_2^{2+}	Orange-coloured ppt.	4.6	The precipitate is soluble in alkalies, as also in *iso*amyl alcohol giving yellow solutions. The coloured species formed in alkaline solution cannot be extracted into organic solvents.
Ti^{4+}	Deep yellow ppt. in acid (H_2SO_4) soln.	3.1	In warm solution precipitation is complete even at 3.2 p_H, but colour of the precipitate is of maximum intensity at 3.6-6.8 p_H. The precipitate is soluble in *iso*amyl alcohol giving a yellow solution in the solvent. The ppt. is decomposed by alkalies.

TABLE I (*contd.*)

Metal-ion.	Nature of reaction.	p_H of incipient pptn. in 0.001*M* soln of metallic ion.	Remarks.
VO_3^-	Greenish black ppt. in acid (H_2SO_4) soln.	2-3	The precipitate is soluble in *iso*amyl alcohol, giving a red-violet solution, but is insoluble in chloroform.
MoO_4^{2-}	Bright yellow colour in slightly acid soln.		The colour is discharged by alkali and excess acid

Copper^{II} *-salicylamidoxime.*—A warm solution of cupric chloride (A. C. S., Merck & Co.), acidified with HCl, was treated with an excess of a little over twice the molar proportion of the amidoxime in 0.1 *N*-HCl, and to this mixture dilute alkali was gradually added to adjust the p_H of the solution to about 4.0-4.5 (tested by B. D. H. indicator paper). The mixture was set aside on the water-bath for about 10 minutes, after which the light green precipitate of the copper compound was filtered. The precipitate was then thoroughly washed with hot water and finally dried to a constant weight at 110°. [Found : N, 15.28 ; Cu, 17.37. Calc. for Cu $(C_7H_7O_2N_2)_2$: N, 15.32 ; Cu, 17.40 per cent].

The substance is light green in colour. It is insoluble in water, but soluble in acids, caustic alkalies and ammonia solutions. It is also somewhat soluble in a hot concentrated solution of sodium acetate or of ammonium chloride. The substance is paramagnetic : $\chi_g = 3.806 \times 10^{-6}$; $\chi_M = 1336.14 \times 10^{-6}$; $\mu_B = 1.81$.

Nickel^{II} *-salicylamidoxime.*— An acidified warm solution of nickel chloride (A. C. S., Merck & Co.) was treated with a little more than twice the molar proportion of the pure amidoxime, dissolved in 0.1 *N*-HCl, and to this mixture dilute ammonia was gradually added to adjust the p_H of the solution to about 7.0-7.5 (tested by B. D. H. indicator paper). The precipitated nickel compound is initially light green in colour, especially if the precipitation starts at not too high a temperature, but readily changes to greyish violet on warming. The mixture was kept on the water-bath for about 10 to 15 minutes and then the precipitated nickel compound was filtered, washed thoroughly with hot water containing a little amount of ammonia (to adjust its p_H to near about 7), and finally dried for one hour to a constant weight at 110°. [Found : N, 15.46 ; Ni, 16.21. Calc. for Ni $(C_7H_7O_2N_2)_2$: N, 15.52 ; Ni, 16.28 per cent].

The substance is greyish violet in colour. It is insoluble in water but soluble in acids, alkalies and ammonia solutions. The compound is diamagnetic : $\chi_g = -0.6521 \times 10^{-6}$; $\chi_M = -235.2 \times 10^{-6}$.

Palladium^{II} *-salicylamidoxime.*—A warm acidified solution of palladous chloride in aqueous sodium chloride was treated with a little over twice the molar proportion of the amidoxime, dissolved in 0.1*N*-HCl, and the p_H was adjusted to 2.5-3.0 by adding KOH solution. The palladium compound was precipitated as a light yellow floppy mass. This was set aside at room temperature for a few minutes, then filtered and the precipitated compound washed thoroughly with hot water and dried at 110°. [Found : N, 13.61 ; Pd, 26.02. Calc. for Pd $(C_7H_7O_2N_2)_2$: N, 13.70 ; Pd, 26.10 per cent]. It is a light yellow powder which is soluble in acids, alkalies and ammonia solutions. The substance is diamagnetic.

Identification Limits of Cu^{II}, Ni^{II}, Bi^{III} *and* Ti^{IV} *by Precipitation with Salicylamidoxime*

A definite volume of the solution of the metal-ion of varying concentrations was treated with an excess of the concentrated amidoxime solution, and the p_H of the resulting mixture was adjusted thereafter, if necessary, by adding acid or alkali as required, for the appearance of any opalescence of the following colours:

Copper	...	greenish white	Bismuth	...	yellowish white
Nickel	...	greyish white	Titanium	...	Do

The smallest amount of the metal required to produce an observable turbidity in each case was determined in this manner. The results are shown below.

TABLE II

Metal ion.	* Identification limit.	† Concentration limit.
Cu^{2+}	1.00 γ (1 c. c.)	$1 : 10^6$
Ni^{2+}	0.60 γ (1 c. c.)	$1 : 1.66 \times 10^6$
Bi^{3+}	20.00 γ (3 c. c.)	$1 : 1.50 \times 10^5$
Ti^{4+}	0.53 γ (0.1 c. c.)	$1 : 1.89 \times 10^5$

* Feigl, *mikrochem.*, 1923, **1**, 4.
† Hahn, *ibid*, 1930, **8**, 75.

Detection of U^{VI}, Fe^{III}, Ti^{IV} *and* V^{V} *by Colour-formation with Salicylamidoxime*

Fe^{III}.—0.005 *M* aqueous solution of salicylamidoxime (5 c. c.) of p_H 9.0-9.5 (adjusted by adding KOH) when treated with 0.1 c. c. of 0.0005 *M* solution of Fe^{3+} (ferric nitrate) was found to be just distinguishable from a blank, prepared identically, but without adding the iron solution. Thus, 2.8γ Fe has been detected. Observations were made lengthwise through the columns of solutions contained in visual colorimeter tubes of 0.45 cm^2. cross-section. The p_H of the solution after the addition of the iron solution should be within the range of 8.3-10.0, which is the optimum p_H range for the colour formation. This has been found out separately.

U^{VI}.—An aqueous solution of salicylamidoxime (0.005 *M*, 5 c. c.) with as little as 0.2 c. c. of 0.005 *M*-$UO_2(NO_3)_2$ at a p_H of 7.9-9.2 produces a yellow colour just distinguishable from the blank; 23.8 γ uranium has thus been detected. Observations were made as in the case of the detection of iron.

Ti^{IV}.—The optimum p_H for the extraction of the yellow precipitate obtained in acid solution has been found to be 3.6-6.8. As little as 2.95 γ Ti can be detected by extracting with 1 c.c. of *iso*amyl alcohol from 15 c.c. of a solution of 0.01*M* in salicylamidoxime and at 4-5 p_H. Observations were made in colorimeter tubes of 0.75 cm^2. cross-section.

V^{V}.—From an acid (H_2SO_4) solution of vanadic acid, at a p_H of 3-4, vanadium is incompletely precipitated. The pink colour formed by the greenish black precipitate on dissolving in *iso*amyl alcohol can be made use of in detecting vanadium. Thus, 2 mg. of vanadium in 5 c. c. of the solution containing excess of salicylamidoxime can be just detected by extraction, at a p_H of 3-4, with 1 c.c. of *iso*amyl alcohol.

Detection of Ti^{IV} *with Salicylaldoxime.*—As little as 2.4γ Ti can be detected by extracting the solution containing excess of the aldoxime, at a p_H of 3·4, with 1 c. c. of chloroform. The optimum p_H for the extraction has been found to be 2.8-7.0.

DISCUSSION

The reactions of salicylamidoxime are comparable to those of the aldoxime (salicylaldoxime), but the p_H values for the incipient precipitation of the metals by the former are somewhat higher. This suggests (cf. Irving and Williams, *Nature*, 1948, **162**, 746 ; Martell and Calvin, "Chemistry of the Metal Chelate Compounds", p. 120, Prentice-Hall, Inc., 1952) that the amidoxime complexes are somewhat less stable than the corresponding aldoxime complexes. A specific influence of the basic $-NH_2$ group in decreasing the strength of the copper specific grouping of the *o*-hydroxyarylaldoximes is thereby indicated. Since such p_H data are not as yet available for salicylhydroxamic acid, a comparison with this substance is not possible at this stage. From the p_H data reported here, the order of stability of the complexes of some common metals can be expressed as: $Pd^{II} > Cu^{II} > UO_2^{II} > Ni^{II} > Fe^{II} > Co^{II} > Zn^{II} > Cd^{II}$. This is more or less the same as that observed, from the p_H data of Flagg and Furman (*loc. cit.*) for the salicylaldoxime complexes.

The p_H of the incipient precipitation, in equimolar solutions, of copper and nickel are more widely different in the case of the amidoxime compared to that for the aldoxime. Furthermore, zinc and cadmium do not form any definite compound with the amidoxime, and their precipitation is prevented altogether in the presence of ammonium chloride. These facts are indicative of a greater selectivity of the amidoxime compared to that of the aldoxime, and thereby furnishes further experimental support to Freiser's view (*Analyst*, 1952, **77**, 830) that organic reagents yielding less stable metal chelates are usually more selective than those giving more stable ones. The identification limits for copper, nickel, bismuth and titanium by precipitation and those of uranium, iron and titanium by colour-formation in suitable solvents with salicylamidoxime are comparable to those for the aldoxime. But for the detection of vanadium the amidoxime is much less sensitive than the aldoxime. This is interesting to note in view of the close analogy found so far between the analytical reactions of the two substances.

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SYNTHESIS OF POLYNUCLEAR HYDROCARBONS WITH FUSED *cyclo*PENTANE RING. PART IV. HYDRINDENE DERIVATIVES BY THE DIELS-ALDER REACTION

By Suresh Chandra Sen Gupta and Anath Jiban Bhattacharyya

The systheses of several hydrindene derivatives, namely 4:7-dimethyl-5:6 diphenyl-, 4:7 diethyl-5:6-diphenyl-, 4-methyl-7-ethyl-5:6 diphenyl- and 4:5:6:7-tetraphenyl-hydrindenes have been carried out by the application of the Diels-Alder reaction. Other attempts in that direction have also been made.

There are comparatively few instances where the Diels-Alder reaction has been utilised for obtaining directly the indene ring system. $\alpha\beta$-Unsaturated cyclic ketones, like 1-methyl-1-*cyclo*penten-5-one and 1-methyl-1-*cyclo*penten-4:5-dione, add with dienes to form indene ring system directly, though in the former case the tendency to form adducts is relatively small (Dane *et al.*, *Annalen*, 1937, **532**, 29; 1939, **537**, 246; 1938, **536**, 196; Bockemüller, *Z. angrew. Chem.*, 1938, **51**, 188). In a previous communication we had shown (this *Journal*, 1954, **31**, 897) that Δ^1-*cyclo*pentene-1:2-dicarboxylic anhydride (II) could be used as an excellent dienophile in the Diels-Alder reaction. We have now utilised this dienophile to obtain the indene ring system directly. The dienophile (II) readily forms adducts with *cyclo*pentadienone derivatives, forming indene ring systems with a carbonyl bridge. The removal of the carbonyl bridge on heating the adduct in a high boiling solvent, like tetralin, followed by decarboxylation, furnishes readily a substituted hydrindene.

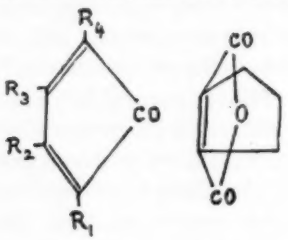
4:7-Dimethyl-5:6-diphenylhydrindene (Va) has been synthesised starting from Δ^1-*cyclo*pentene-1:2-dicarboxylic anhydride (II) and the dimer of 2:5-dimethyl-3:4-diphenyl*cyclo*pentadienone (Ia). The dienone dimer dissociates into the monomer in boiling xylene solution and forms the adduct 4:7:8:9-tetrahydro-4:7-dimethyl-5:6-diphenyl-4:7-endocarbonyl-hydrindene-8:9-dicarboxylic anhydride (IIIa). This adduct readily loses the carbonyl bridge when heated at the temperature of boiling tetralin solution, forming 8:9-dihydro-4:7-dimethyl-5:6-diphenylhydridene-8:9-dicarboxylic anhydride (IVa). The latter on distillation with soda-lime is decarboxylated and dehydrogenated, yielding 4:7-dimethyl-5:6-diphenylhydrindene (Va).

In a similar manner 4:7-diethyl-5:6-diphenylhydrindene (Vb) has been synthesised, starting from 2:5-diethyl-3:4-diphenyl*cyclo*pentadienone (Ib) and the anhydride (II). The adduct (IIIb) is readily formed when these two components are heated in xylene solution. The same adduct has also been obtained when $\alpha\beta$-diethylanhydroacetone-benzil, the carbinol, from which the dienone (Ib) is prepared, is taken in place of the dienone (Ib) and the reaction is conducted in acetic anhydride solution with the addition of a few drops of sulphuric acid. Under this condition the dienone (Ib) is formed and adds to the dienophile (II) present in the solution. The adduct (IIIb) has been converted into 4:7-diethyl-5:6-diphenylhydrindene (Vb) under the conditions used for converting

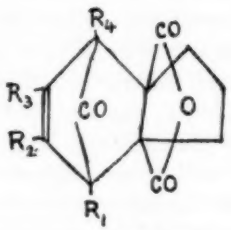
(IIIa) to (Va). 4-Methyl-7-ethyl-5:6-diphenylhydriudene (Vc) has also been sythesised starting from 2-methyl-5-ethyl-3:4-diphenyl*cyclo*pentadienone (Ic) and the anhydride (II).

During the synthesis of 4 : 5 : 6 : 7-tetraphenylhydrindene (Vd) it has been noted that the dienone, tetracyclone (Ib), and the anhydride (II) react in boiling xylene solution, affording directly the decarbonylated adduct (IVd). The product (IVd) when heated with soda-lime furnishes 4 : 5 : 6 : 7-tetraphenylhydrinedene (Vd), identical with that obtained by Grumitto *et al.* (*J. Amer. Chem. Soc.*, 1942, **64**, 604).

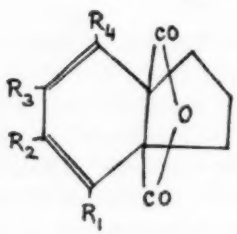
Anisylcyclone (Ie) and piperylcyclone (If) readily form adducts when heated respectively in boiling xylene solution with the anhydride (II). In the former case, the adduct (IIIe) retains the carbonyl bridge, whereas in the latter case the carbonyl bridge is lost during the reaction in boiling xylene, and the product isolated is (IVf). The adduct (IIIe) loses CO when heated in tetralin solution at 200°, affording (IVe). These two decarbonylated adducts could not be satisfactorily decarboxylated by heating with soda-lime, and the corresponding hydrindene derivatives have not been isolated.



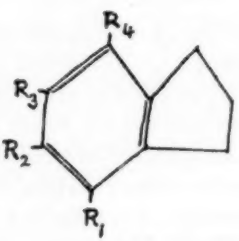
(I) (II)



(III)

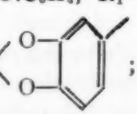


(IV)



(V)

a : $R_2=R_3=Ph$; $R_1=R_4=Me$.
b : $R_2=R_3=Ph$; $R_1=R_4=Et$.
c : $R_2=R_3=Ph$; $R_1=Me$; $R_4=Et$.
d : $R_1=R_2=R_3=R_4=Ph$.
e : $R_2=R_3=p$-MeO.C_6H_4; $R_1=R_4=Ph$.

f : $R_2=R_3=CH_2$  ; $R_1=R_4=Ph$.

EXPERIMENTAL

4:7:8:9-Tetrahydro-4:7-dimethyl-5:6-diphenyl-4:7-endocarbonylhydrindene-8:9-dicarboxylic Anhydride (IIIa).—The dimer of 2:5-dimethyl-3:4-diphenyl*cyclo*pentadienone, required for this experiment, was prepared by the dehydration of αβ-dimethylanhydroacetone-benzil (Gray, *J. Chem. Soc.*, 1909, **95**, 2134) and the latter was prepared from benzil and diethylketone (Japp and Meldrum, *ibid.*, 1901, **79**, 1031). The dimer of 2:5-dimethyl-3:4-diphenyl*cyclo*pentadienone (Ia; 10 g.) and the anhydride of Δ^1-*cyclo*pentene-1:2-dicarboxylic acid (II ; 8 g.) were heated in xylene solution at 140°-145° (bath temperature) until the red colour of the solution almost had disappeared (4 hours). It was then allowed to stand overnight when the adduct separated. It was crystallised from benzene, m.p. 217-18° (decomp.), yield 6.8 g. (Found : C, 78.3. H, 5.9 ; $C_{26}H_{22}O_4$ requires C, 78.3; H, 5.5 per cent).

8:9-Dihydro-4:7-dimethyl-5:6-diphenylhydrindene-8:9-dicarboxylic Anhydride (IVa).—The adduct (IIIa ; 5 g.) was refluxed in tetralin (15 c.c.) solution until the evolution of CO had ceased (about 2 hours). Tetralin was removed by steam-distillation and the residue was crystallised from benzene-alcohol mixture, m.p. 205°, yield 3 g. (Found : C, 80.66 ; H, 6.2. $C_{25}H_{22}O_3$ requires C, 81.08 ; H, 5.94 per cent).

4:7-Dimethyl-5:6-diphenylhydrindene (Va).—The bridgeless adduct (IV a ; 5 g.) was mixed with soda-lime (8 g.) and heated in a Pyrex test tube under slightly reduced pressure when a liquid distillate (2 g.) was obtained. This slowly solidified. It was crystallised from rectified spirit, m.p. 139°. (Found : C, 92.62; H, 7.8. $C_{23}H_{22}$ requires C, 92.61; H, 7.38 per cent).

4:7:8:9-Tetrahydro-4:7-diethyl-5:6-diphenyl-4:7-endocarbonylhdrindene-8:9-dicarboxylic Anhydride (IIIb).—Diethyldiphenyl*cyclo*pentadienone (Ib), required here, was prepared from αβ-diethylanhydroacetone-benzil (Allen and Van Allan, *J. Amer. Chem. Soc.*, 1950, **72**, 5166; Japp and Meldrum, *J. Chem. Soc.*, 1901, **79**, 1040).

(A). Diethyldiphenyl*cyclo*pentadienone (Ib ; 10 g.) and Δ^1-*cyclo*pentene-1:2-dicarboxylic anhydride (II ; 8 g.) in xylene (25 c.c.) were heated as described before. The adduct was washed with a little spirit and crystallised from benzene, m.p. 170° (decomp.), yield 6 g. (Found : C, 78.24 ; H, 6.3. $C_{28}H_{26}O_4$ requires C, 78.8 ; H, 6.1 per cent).

(B). To a solution of αβ-diethylanhydroacetone-benzil (5 g.) and Δ^1-*cyclo*pentene-1:2-dicarboxylic anhydride (3 g.) in acetic anhydride (20 c.c.) were added a few drops of H_2SO_4 (conc.). An exothermic reaction set in and the adduct separated after an hour. The reaction mixture was treated with water and the separated solid was crystallised from benzene, m.p. 170° (decomp.), yield 3.5 g. The mixed m.p. with a sample prepared by method (A) remained unaltered.

8:9-Dihydro-4:7-diethyl-5:6-diphenylhydrindene-8:9-dicarboxylic Anhydride (IVb).—The adduct (IIIb; 5 g.) was decarbonylated as in the case of (IIIa), and the product was crystallised from alcohol, m.p. 156°, yield 3.5 g. (Found : C, 81.22 ; H, 6.9. $C_{27}H_{26}O_3$ requires C, 81.4; H, 6.54 per cent).

4 : 7-*Diethyl*-5 : 6-*diphenylhydrindene* (Vb).—The bridgeless adduct (IVb; 5 g.) was heated with soda-lime (8 g.), as described before, when a liquid distillate was obtained. This was triturated with a little alcohol when it solidified. The hydrocarbon was crystallised from rectified spirit in needles, m.p. 128°, yield 1.5 g. (Found : C, 91.79; H, 8.25. $C_{25}H_{26}$ requires C, 92.02; H, 7.97 per cent).

2-*Methyl*-5-*ethyl*-3:4-*diphenyl*cyclo*pentadienone* (Ic).—The dienone was prepared according to the general procedure outlined by Allen and Van Allan (*loc. cit*.) for the preparation of *cyclo*pentadienones. Benzil (42 g.) and *n*-propylethyl ketone (40 g.) were added to 500 c.c. of 0.5 % absolute alcoholic KOH solution, shaken and allowed to stand for 4 days. It was diluted with water, the separated oil extracted with benzene, dried and the solvent removed. The residual oil (35 g.) was mixed with acetic anhydride (60 c.c.) and a few drops of H_2SO_4 (conc.). Much heat was evolved and the mixture was allowed to stand for 12 hours at the ordinary temperature. The separated solid was washed with spirit and crystallised from alcohol, m.p. 140° (decomp.), shrinking earlier, yield 18 g. This was evidently obtained as the dissociating dimer (Allen and Van Allan, *loc. cit*.). (Found : C, 87.43; H, 6.79. $C_{20}H_{18}O$ requires C, 87.59; H, 6.56 per cent).

4 : 7 : 8 : 9 *Tetrahydro*-4-*methyl*-7-*ethyl*-5 : 6-*diphenyl*-4 : 7-*endocarbonylhydrindene*-8 : 9-*dicarboxylic Anhydride* (IIIc).—2-Methyl-5-ethyl-3 : 4-diphenyl*cyclo*pentadienone (Ic; 8 g.) and the anhydride (II; 8 g.) in xylene (25 c.c.) were heated as before and the separated adduct was crystallised from benzene, m. p. 250° (decomp.), yield 5 g. (Found: C, 78.5; H, 5.8. $C_{27}H_{24}O_4$ requires C, 78.6; H, 5.8 per cent).

8:9-*Dihydro*-4-*methyl*-7-*ethyl*-5:6-*diphenylhydrindene*-8 : 9 - *dicarboxylic Anhydride* (IVc).—The adduct (IIIc; 5 g.) was decarbonylated in tetralin solution and crystallised from alcohol, m.p. 194°, yield 3 g. (Found : C, 81.61 ; H, 6.6. $C_{26}H_{24}O_3$ requires C, 81.25; H, 6.25 per cent).

4-*Methyl*-7-*ethyl*-5 : 6-*diphenylhydrindene* (Vc).—The decarbonylated product (IVc ; 5 g.) was heated with soda-lime (8 g.) as described before. A liquid distillate was obtained, which slowly solidified and was crystallised from alcohol in stout needles, m.p. 105°. (Found : C, 92.6; H, 7.44. $C_{24}H_{24}$ requires C, 92.31 ; H, 7.69 per cent).

8 : 9-*Dihydro*-4:5 : 6:7-*tetraphenylhydrindene*-8 : 9-*dicarboxylic Anhydride* (IVd).—Tetracyclone (Id; 10 g.) (Dilthey and Quint, *J. prakt. Chem*.. 1930, **128**, 139) and the anhydride (II; 6 g.) in xylene (25 c.c.) were refluxed until the dark violet colour of the ketone almost had disappeared (about 3 hours). Carbon monoxide was evolved during the reaction. On standing the colorless adduct slowly separated out. This was collected, washed with a little benzene to remove unchanged ketone and crystallised from benzene, m.p. 263-64°, yield 8 g. (Found : C, 84.6; H, 5.21. $C_{35}H_{26}O_3$ requires C, 85.0; H, 5.2 per cent).

4 : 5 : 6 : 7-*Tetraphenylhydrindene* (Vd).—The adduct (IVd ; 5 g.) and soda-lime (8 g.) were heated as described before. A solid sublimate was obtained. It was crystallised from benzene-hexane mixture, m.p. 223°. (Grumitto *et al*., *loc. cit*., record m.p. 225°). (Found : C, 94.2; H, 6.6. Calc. for $C_{33}H_{26}$: C, 93.83; H, 6.16 per cent).

4 : 7 : 8 : 9-*Tetrahydro*-4 : 7-*diphenyl*-5 : 6-*di*-p-*anisyl*-4 : 7-*endocarbonyl-hydrindene*-8 : 9-*dicarboxylic Anhydride* (IIIe).—Anisylcyclone (10 g.) (Dilthey *et al.*, *J. prakt. Chem.*, 1934, **141**, 331) and the anhydride (II ; 6 g.) in dry xylene (30 c.c.) were heated and worked up as described before. The separated adduct was washed with a little cold benzene to remove the traces of anisylcyclone and was crystallised from benzene in colorless cubes, m.p. 138-39° (decomp.). (Found : C, 78.7; H, 5.6. $C_{38}H_{30}O_6$ requires C, 78.3; H, 5.15 per cent).

8 : 9-*Dihydro*-4 : 7-*diphenyl*-5 : 6-*di*-p-*anisylhydrindene*-8 : 9-*dicarboxylic Anhydride* (IVe).—The adduct (IIIe; 4 g.) was decarbonylated in tetralin solution. The product was washed with a little cold benzene and crystallised from benzene, m.p. 202°, yield 2.5 g. (Found : C, 79.91 ; H, 5 6. $C_{37}H_{30}O_5$ requires C, 80.14; H, 5 4 per cent).

8 : 9-*Dihydro*-4 : 7-*diphenyl*-5 : 6-bis-*dioxymethylenephenylhydrindene*-8 : 9-*dicarboxylic Anhydride* (IVf).—Piperylcyclone (If; 8 g.) (Arbuzov and Akhmed-Zade, *J. Gen. Chem.*, *U.S.S.R.* 1942, **12**, 212) and the anhydride (II; 5 g.) in xylene (25 c.c.) were heated as before. Carbon monoxide was liberated during the reaction. The mixture was allowed to stand overnight when the adduct separated out. It was collected, washed with benzene to remove traces of piperylcyclone and crystallised from benzene, m.p. 262° (decomp.), yield 4 g. (Found : C, 75.7; H, 4.7. $C_{37}H_{26}O_7$ requires C, 76.28 ; H, 4.46 per cent).

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MALATE COMPLEX OF TRIVALENT ANTIMONY

By Ch. B. Nanda and S. Pani

The evidence of the existence of a malate complex of trivalent antimony (complex III) containing one malate ligand per atom of antimony has been obtained by the solubility method. The equilibrium constant of the reaction by which the complex is formed from the antimonyl ion and malate ion has been determined. The mean value of the constant is 1.730×10^7.

Attempts have been made (Henderson and Barr, *J. Chem. Soc.*, 1896, **69**, 1452; Brahmachari, *Indian J. Med. Res.*, 1923, **11**, 207) to prepare antimonyl malates by refluxing antimony oxide with aqueous solutions of bimalates. Different investigators appear to have secured different products.

Citrate ligand has recently been found to occupy three co-ordinate positions in antimony citrate complex (Das and Pani, this *Journal*, 1955, **32**, 537).

In malic acid the asymmetric carbon atom is joined to one -COOH, one -OH, one $-CH_2CO_2H$ and one H atom. If the hydrogen atom is replaced by another $-CH_2CO_2H$ group, citric acid is obtained. It has been seen from the quantitative investigations carried out in this laboratory that the α-hydroxy group and the carboxyl group (to which the hydroxyl group is in α-position) are most suitable for the formation of a five-membered ring with antimony.

Since the citrate ligand occupies three co-ordinate positions, the carboxyl group to which the hydroxyl group is in α-position, the hydroxyl group and one of the remaining carboxyl groups react with the antimony atom and there are one five-and one six-membered ring. It can, however, be possible that there are two six-membered rings. To verify this, it was thought worthwhile to investigate the complex of antimony with malic acid. If two six-membered rings are favoured, malate ligand would be bidentate, and accordingly a malate complex containing two malate ligands per atom of antimony would be formed. If, however, the formation of a five- and a six-membered ring is favoured, the malate ligand would be tridentate, and 1:1 complex would be formed, since the co-ordination number of antimony is found to be four in all complexes with hydroxyl and polybasic acids (this *Journal*, 1954, **31**, 588, 593; 1955, **32**, 217).

Experimental

Approximately a 0.25*M* solution of malic acid was prepared and standardised against standard NaOH solution (standardised against a standard succinic acid solution). A known volume of the malic acid solution was taken and the calculated amount of NaOH was added to neutralise the acid to definite extents (1/6, 1/4, 1/3, 1/2, 3/4). The neutralised

solution was then diluted to different extents. The solubility of antimony oxide in these solutions was determined at 35° after Das and Pani (*loc. cit.*). The antimony contents of the solutions were determined by titrating a known volume of the solutions against a standard bromate solution. The p_H was measured by a Marconi p_H-meter. The results are recorded in Table I.

TABLE I

Series.	[Ml].	$[MlOH^{2-}]\times10^2$.	[SbC].	p_H.	$K\times10^{-7}$.	K_b
	0.1125	5.676	0 01372	4.82	2.073	2.876×10^7
	0.1000	5.960	0.01150	5.00	2.506	5.262
	0.0875	5.072	0 00912	4.95	2.081	3.895
3/4	0.0650	3.854	0.00686	4.98	2.208	4.428
	0.0525	3.032	0.00526	4.94	1.964	3.592
	0 0400	2.317	0.00381	4.86	1.654	2 516
	0.1125	1.926	0.01809	4.14	2.121	6.146×10^6
	0.1000	1.401	0.01506	4.04	1.531	3.525
	0.0875	1.377	0 01269	4.08	1.439	3.632
1/2	0.0650	0.659	0.00988	3.90	1.547	2.580
	0.0525	0.693	0.00857	4.02	1.681	3.697
	0 0400	0.561	0.00601	4.04	1.527	3.515
	0.1125	1.234	0.01861	3.94	1.707	3.121×10^6
	0.1000	1.162	0.01560	3.96	1.585	3.035
	0.0875	1.038	0.01383	3.97	1.614	3.162
1/3	0.0650	0.790	0.01025	3.98	1.609	3.227
	0.0525	0.668	0.00826	4.00	1.607	3.375
	0.0400	0.532	0.00628	4.02	1.603	3.526
	0.1125	0.477	0.01954	3.58	2.024	1.617×10^6
	0.1000	0.455	0.01840	3.61	2.137	1.828
	0.0875	0.413	0.01560	3.62	2.044	1.789
1/4	0.0650	0.343	0.01166	3.66	2.019	1.938
	0.0525	0.307	0.01000	3.68	2.022	2.033
	0.0400	0.218	0.00699	3.67	1.946	1.912
	0.1125	0.182	0.01614	3.03	1.235	2.778×10^6
	0.1000	0.162	0.01407	3.03	1.208	2.715
	0.0875	0.124	0.01249	2.98	1.260	2.506
1/6	0.0650	0.056	0.01000	3.00	1.351	2.837
	0.0525	0.081	0.00782	3.02	1.294	2.845
	0.0400	0.069	0.00606	3.06	1.304	3.145

There are two possibilities of the reaction, namely, the ligand may behave as bidentate like lactate, or tridentate like citrate. Besides, bimalate or the malate ions might be taking part in the reaction. It is therefore necessary to take all the possible reactions into account. The following four reactions, (*a*), (*b*), (*c*) and (*d*), are possible, assuming antimonyl ion (SbO^+) to be reacting with n bimalate ions ($HMlOH^-$) or n malate ($MlOH^{2-}$) ions and the ligands are bidentate or tridentate. The equilibrium constants are given by the equations (*a*-1), (*b*-1), (*c*-1) and (*d*-1) respectively.

$$SbO^+ + n\ HMlOH^- \rightleftharpoons \left[Sb\left(\begin{array}{l} O-C=O \\ | \\ O-CH \\ | \\ CH_2-COOH \end{array} \right)_n \right]^{+3-2n} + (n-2)H^+ + H_2O \quad \ldots \quad (a)$$

$$\frac{[SbC] \times [H^+]^{(n-2)}}{[SbO^+] \times [HMlOH^-]^n} = K_a \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (a-1)$$

$$SbO^+ + n\ HMlOH^- \rightleftharpoons \left[Sb\left(\begin{array}{l} O-C=O \\ | \\ O-CH \\ | \\ O-C \\ \| \\ O \end{array} \right)_n \right]^{+3-3n} + (2n-2)\ H^+ + H_2O \quad \ldots \quad (b)$$

$$\frac{[SbC] \times [H^+]^{(2n-2)}}{[SbO^+] \times [HMlOH^-]^n} = K_b \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (b-1)$$

$$SbO^+ + n\ MlOH^{2-} \rightleftharpoons \left[Sb\left(\begin{array}{l} O-C=O \\ | \\ O-CH \\ | \\ CH_2COO \end{array} \right)_n \right]^{+3-3n} + (n-2)\ H^+ + H_2O \quad \ldots \quad (c)$$

$$\frac{[SbC] \times [H^+]^{(n-2)}}{[SbO^+] \times [MlOH^{2-}]^n} = K_c \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (c-1)$$

$$SbO^+ + n\ MlOH^{2-} \rightleftharpoons \left[Sb\left(\begin{array}{l} O-C=O \\ | \\ O-CH \\ | \\ O-C \\ \| \\ O \end{array} \right)_n \right]^{+3-3n} + (n-2)\ H^+ + H_2O \quad \ldots \quad (d)$$

$$\frac{[SbC] \times [H^+]^{(n-2)}}{[SbO^+] \times [MlOH^{2-}]^n} = K_d \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (d-1)$$

$[SbC]$, $[HMlOH^-]$, $[MlOH^{2-}]$, $[H^+]$ and $[SbO^+]$ represent the molar concentration of the complex, bimalate ion, malate ion, hydrogen ion and antimonyl ion respectively. It is assumed that only one of the above reactions takes place and the complex (SbC) is formed. The equilibrium constants of the reactions (*c*) and (*d*) are the same; it is therefore not possible to judge from the constancy of the equilibrium constant the number of co-ordination positions occupied by the malate ligand. If the complex is 1:1, the malate

ligand most probably occupies more than two, *i.e.* three, positions in the co-ordination sphere. If, however, the complex contains two malate ligands per atom of antimony, the malate ligand would be expected to be bidentate.

In each set of experiments the p_H is very nearly constant. Taking the p_H to be constant and substituting $[SbO^+]$ by $7.7 \times 10^{-4} \times [H^+]$ (*J. Amer. Chem. Soc.*, 1952, **74**, 2353), it can be shown that the equation (I) holds for reactions (*a*) and (*b*) for each set of experiments.

$$\frac{[SbC]}{[HMlOH^-]^n} = K_1 \quad \ldots \quad \ldots \quad \ldots \quad (I)$$

Substituting the value of SbO^+ in equation (*c*-1) or (*d*-1) and $[MlOH^{2-}]$ by $k_2 \times [HMlOH^-]/[H^+]$, where k_2 is the second dissociation constant of malic acid, t can be shown that equation (I) also holds for the reactions (*c*) and (*d*) for each set of experiments. Taking the logarithm of both sides, the equation (I) can be written as

$$\log [SbC] = \log K_1 + n \log [HMlOH^-] \quad \ldots \quad \ldots \quad (I\text{-}1)$$

If log [SbC] is plotted against log $[HMlOH^-]$, a straight line would be obtained and the slope would give the value of n.

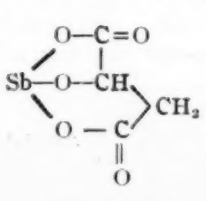
Since the solubility of antimony oxide in water is very small, the whole of the antimony in the solution is assumed to be present as a complex. The total malate [Ml] in the solution is present as undissociated malic acid (H_2MlOH), bimalate ion, malate ion and the malate present in the complex. Hence,

$$[Ml] = [H_2MlOH] + [HMlOH^-] + [MlOH^{2-}] + n\,[SbC] \quad \ldots \quad (I\text{-}2)$$

or,
$$[Ml] - n\,[SbC] = [HMlOH^-] \times \{([H^+]/k_1) + 1 + k_2/[H^+]\} \quad \ldots \quad (I\text{-}3)$$

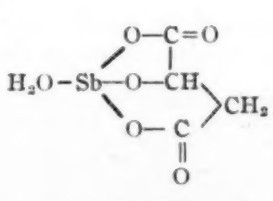
where k_1 and k_2 are the first and the second dissociation constants of malic acid. Taking k_1 and k_2 to be 5.5×10^{-4} and 2.1×10^{-5} (Cannon and Kibrick, *J. Amer. Chem. Soc.*, 1938, **60**, 814) respectively and assuming n to be equal to 1 and 2, two sets of values of $[HMlOH^-]$ are calculated. The two sets of values do not differ much since [SbC] is small compared to [*Ml*], and the differences in the log values are still smaller. The log [SbC] values are plotted against the corresponding log $[MHlOH^-]$ values. Very nearly staright lines are obtained in both the cases and the slope is very nearly 1 in all the four sets of experiments. The complex therefore contains one malate ligand per atom of antimony and the ligand is most probably tridentate.

The reaction (*b*) or (*d*) might be taking place. The complex formed by the equation (*b*) might be complex (I) or (II), as shown below :



(Complex I)

or



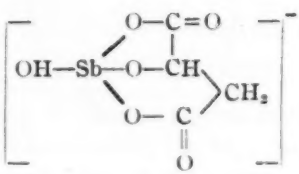
(Complex II)

In either case of the formation of complex (I) or complex (II), no hydrogen ion would be liberated due to the reaction between antimonyl and bimalate ions. The value of the equilibrium constant would be the same.

The latter structure would, however, arise if the co-ordination number of antimony is four. The complex being a neutral molecule would be very little soluble. By substituting the value of n by 1, the equilibrium constant K_b is calculated. The values are fairly constant in each set of experiments (p_H is constant) but vary from one set to another set. K_b is therefore variable and the reaction (*b*) probably does not take place.

If the reaction (*d*) is considered, it becomes obvious that a malate ligand would furnish only one hydrogen ion, and it would not be possible to remove the oxygen atom of the antimonyl ion as water molecule. Therefore, a hydroxyl group would remain attached to the antimony atom. It might also be possible that a hydroxyl group would be liberated due to the formation of the complex. The latter appears to be less probable since the solubility of antimony oxide at the beginning increases with increasing p_H. This latter complex would be the same as complex (I), supposed to be formed by the interaction of antimonyl ion with bimalate ion. It is therefore not necessary to consider this again since it can be shown that the value of the equilibrium constant would be a constant multiple of K_b. It is therefore assumed that hydroxyl group remains attached to the antimony atom. The reaction is represented by equation (II) and the equilibrium constant K by equation (II·1).

$$SbO^+ + MlOH^{2-} \rightleftharpoons$$



... ... (II)

(Complex III)

$$\frac{[SbC]}{7.7 \times 10^{-4} \times [H^+] \times [MlOH^{2-}]} = K \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (II\text{-}1)$$

The values of K are shown in Table I. It is interesting to note that the values are not only constant at a constant p_H but remain constant throughout the p_H range of investigation. The complex is therefore represented by complex (III) and the reaction, by equation (II).

The mean value of the equilibrium constant is 1.730×10^7. The results obtained support the structure of the citrate complex proposed by Das and Pani (*loc. cit.*).

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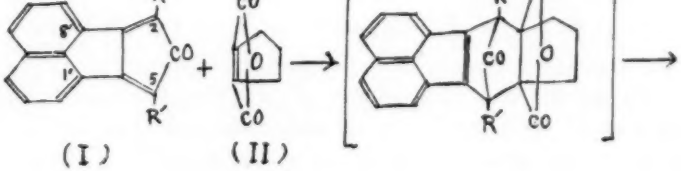
SYNTHESIS OF POLYNUCLEAR HYDROCARBONS WITH FUSED *cyclo*PENTANE RING. PART V. *cyclo*PENTENO-FLUORANTHENE DERIVATIVES

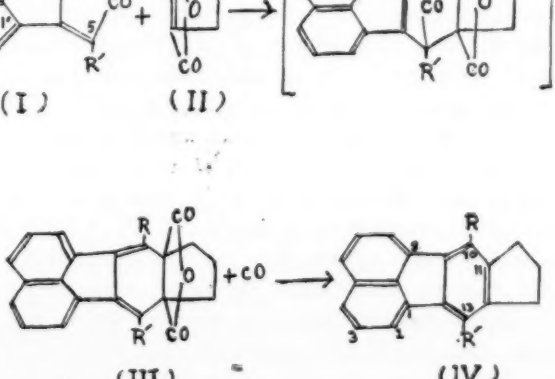
By Suresh Chandra Sen Gupta and Anath Jiban Bhattacharyya

The syntheses of several dialkyl- and diaryl-11:12-*cyclo*pentenofluoranthenes have been carried out by the application of the Diels-Alder reaction.

A very convenient procedure for the synthesis of fluoranthene derivatives is that used by Dilthey by the application of the Diels-Alder reaction. He treated the *cyclo*pentadienone derivative, acecyclone (I : R = R′ = Ph), with maleic anhydride and other dienophiles when fluoranthene derivatives were formed by the loss of the carbonyl bridge of the adduct. 10 : 11 : 12 : 13-Tetraphenylfluoranthene had been synthesised starting from acecyclone and tolane (Dilthey, Henkels and Schäfer, *Ber.*, 1938, **71**, 974). By an extension of this procedure Allen and Van Allan (*J. Org. Chem.*, 1952, **17**, 845) have synthesised a large number of substituted fluoranthenes. We have in the present investigation utilised this method for the synthesis of a number of substituted 11 : 12-*cyclo*pentenofluoranthenes (IV).

When acecyclone (I : R = R′ = Ph) was taken as the diene component and Δ^1-*cyclo*pentene-1 : 2-dicarboxylic anhydride (II) as the dienophile, they readily formed an adduct from which the endocarbonyl bridge was eliminated at the temperature of the reaction that was carried out in boiling xylene solution. The decarbonylated adduct (III : R = R′ = Ph), so obtained, was decarboxylated and dehydrogenated by distillation with soda-lime under slightly reduced pressure when 10 : 13-diphenyl-11 : 12-*cyclo*pentenofluoranthene (IV : R = R′ = Ph) was obtained.





In place of acecyclone, the dimers of 2:5-dialkyl*cyclo*pentadienones (I: R=R′= alkyl) had also been used. The dimer dissociated to the monomer (Allen and Van Allan, *loc. cit.*) and the latter then formed the adduct. By following this procedure 10:13-dimethyl-, 10:13-diethyl- and 10-methyl-13-ethyl-11:12-*cyclo*pentenofluoranthenes (IV: R=R′=Me or Et and R=Me; R′=Et) had been synthesised starting respectively from the dimers of 2:5-dimethyl-, 2:5-diethyl- and 2-methyl-5-ethyl-3:4-(1′:8′-naphthylene)-*cyclo*pentadienone (I: R=R′=Me or Et, and R=Me; R′=Et) and the dienophile, Δ^1-*cyclo*pentene-1:2-dicarboxylic anhydride (II). These hydrocarbons are all light yellow substances.

2:5-Di-*p*-tolyl-3:4-(1′:8′-naphthylene)-*cyclo*pentadienone (I: R=R′=*p*-tol) and Δ^1-*cyclo*pentene-1:2-dicarboxylic anhydride (II) formed the adduct (III: R=R′=*p*-tol). This adduct has not been decarboxylated to the corresponding hydrocarbon.

EXPERIMENTAL

11:12-*Dihydro*-10:13-*diphenyl*-11:12-cyclo*pentenofluoranthene*-11:12-*dicarboxylic Anhydride* (III: R=R′=Ph).—Acecyclone (I: R=R′=Ph) (Dilthey, ter Horst and Schommer, *J. prakt. Chem.*, 1935, **143**, 189) (15 g.) and Δ^1-*cyclo*pentene-1:2-dicarboxylic anhydride (II; 8 g.) in dry xylene (40 c.c.) were refluxed in a glycerine bath at 150°-155° (bath temperature) until the evolution of carbon monoxide had ceased (about 6 hours). The reaction mixture was then cooled and allowed to stand. The separated product was filtered, washed with a little benzene and crystallised from a large volume of benzene, m.p. 269°, yield 9 g. (Found: C, 85.0; H, 4.4. $C_{33}H_{22}O_3$ requires C, 84.9; H, 4.7 per cent). Benzene-insoluble product (2 g.) was left. This was not a sharp melting substance and was evidently a polymerised product.

10:13-*Diphenyl*-11:12-cyclo*pentenofluoranthene* (IV: R=R′=Ph).—The adduct (III: R=R′=Ph) (5 g.) was mixed with soda-lime (8 g.) and heated in a long Pyrex test tube under reduced pressure. A yellow sublimate (2 g.) with a green fluorescence condensed on the cooler end of the tube. The sublimate was purified by repeated crystallisation from hexane and obtained as stout pale yellow needles, m.p. 217-18°. (Found: C, 94.09; H, 5.9. $C_{31}H_{22}$ requires C, 94.41; H, 5.58 per cent).

11:12-*Dihydro*-10:13-*dimethyl*-11:12-cyclo*pentenofluoranthene*-11:12-*dicarboxylic Anhydride* (III: R=R′=Me).—The dimer of 2:5-dimethyl-3:4-(1′:8′-naphthylene)-*cyclo*pentadienone (I: R=R′=Me) (10 g.) (Allen and Van Allan, *J. Org. Chem.*, 1952, **17**, 852) and Δ^1-*cyclo*pentene-1:2-dicarboxylic anhydride (II; 7 g.) in xylene (30 c.c.) were heated as before until evolution of carbon monoxide had ceased (4 hours). The separated adduct crystallised from acetic anhydride or benzene in needles, m.p. 233°, yield 6 g. (Found: C, 80.35; H, 5.2. $C_{23}H_{18}O_3$ requires C, 80.7; H, 5.2 per cent).

10:13-*Dimethyl*-11:12-cyclo*pentenofluoranthene* (IV: R=R′=Me).—The adduct (III: R=R′=Me) (6 g.) and soda-lime (8 g.) were heated under reduced pressure. A yellow sublimate (2.5 g.) was obtained. It was crystallised from hexane and melted unsharply at 165°. It was purified through the picrate, which was obtained as deep orange needles from absolute alcoholic solution, m.p. 203°-204°. The picrate dissociated on recrystallisation from alcohol. (Found: C, 64.6; H, 3.9. $C_{27}H_{21}O_7N_3$

requires C, 64.93; H, 4.2 per cent). The hydrocarbon was regenerated from the picrate and crystallised from alcohol in yellow flakes, m.p. 178°. (Found: C, 92.98; H, 6.99. $C_{21}H_{18}$ requires C, 93.33; H, 6.66 per cent).

The *dimer of* 2-*methyl*-5-*ethyl*-3:4-(1′:8′-*naphthylene*)-cyclo*pentadienone* (I:R=Me; R′=Et) was prepared exactly as in the case of the dimer of (I: R=R′=Me) (Allen and Van Allan, *loc. cit.*) starting from acenaphthenequinone and *n*-propylethyl ketone. The carbinol, first prepared from these two, crystallised from alcohol in needles, and was obtained as a mixture of isomers, m.p. 180-81°, sintering earlier. (Found: C, 81.7; H, 6.1. $C_{18}H_{16}O_2$ requires C, 81.81; H, 6.06 per cent). The dienone was obtained as dimer by dehydration of the carbinol in acetic anhydride solution with the addition of a few drops of H_2SO_4 (conc.). It crystallised from benzene, m.p. 190°, sintering earlier. (Found: C, 87.8; H, 6.0. $C_{18}H_{14}O$ requires C, 87.8; H, 5.7 per cent).

11:12-*Dihydro*-10-*methyl*-13-*ethyl*-11:12-cyclo*pentenofluoranthene*-11:12-*dicarboxylic Anhydride* (III:R=Me; R′=Et).—The above dimer (I: R=Me; R′=Et) (12 g.) and Δ^1-*cyclo*penteno-1:2-dicarboxylic anhydride (8 g.) were heated in xylene solution, as described before. The adduct was crystallised from benzene, m.p. 174°, yield 6 g. It gave a pinkish fluorescence in benzene solution. (Found: C, 81.0; H, 5.8. $C_{24}H_{20}O_3$ requires C, 80.89; H, 5.61 per cent).

10-*Methyl*-13-*ethyl*-11:12-cyclo*pentenofluoranthene* (IV: R=Me; R′=Et).—The adduct (III: R=Me; R′=Et) (6 g.) was heated with soda-lime (8 g.), as described before, when a liquid distillate was obtained. The distillate solidified on trituration with a little alcohol. On crystallisation from alcohol an unsharp melting substance was obtained. This was converted into the picrate in absolute alcoholic solution as deep orange needles, m.p. 176°. (Found: C, 65.3; H, 4.5. $C_{28}H_{23}O_7N_3$ requires C, 65.49; H, 4.48 per cent). The hydrocarbon was regenerated from the picrate and crystallised from alcohol as a pale yellow substance, m.p. 132°. (Found: C, 92.89; H, 7.0. $C_{22}H_{20}$ requires C, 92.95; H, 7.0 per cent).

11:12-*Dihydro*-10:13-*diethyl*-11:12-cyclo*pentenofluoranthene*-11:12-*dicarboxylic Anhydride* (III: R=R′=Et).—The dimer of 2:5-diethyl-3:4-(1′:8′-naphthylene)-*cyclo*pentadienone (I: R=R=Et) (10 g.) (Allen and Van Allan, *loc. cit.*) and Δ^1-*cyclo*pentene-1:2-dicarboxylic anhydride (7 g.) in xylene (30 c.c.) were heated, as described before. The adduct was washed with a little spirit and crystallised from benzene in cubes, m.p. 158°, yield 5.5 g. Freshly crystallised adduct was colorless but on keeping in air it acquired a pale pink colour. In most of the organic solvents it gave a light violet fluorescence. (Found: C, 81.07; H, 6.1. $C_{25}H_{22}O_3$ requires C, 81.09; H, 5.9 per cent).

10:13-*Diethyl*-11:12-cyclo*pentenofluoranthene* (IV: R=R′=Et).—The adduct (III: R=R′=Et) (6 g.) was heated with soda-lime (8 g.) as, described before. A yellow sublimate (2.5 g.) was obtained. This was converted into picrate in absolute alcoholic solution as shining red needles, m.p. 174°. (Found: C, 65.8; H, 4.8. $C_{29}H_{25}O_7N_3$ requires C, 66.03; H, 4.74 per cent). The hydrocarcon was regenerated from the picrate and crystallised from alcohol in light yellow needles, m.p. 142°. (Found: C, 92.42; H, 7.42. $C_{23}H_{22}$ requires C, 92.61; H, 7.38 per cent).

2 : 5-*Di*-p-*tolyl*-3:4-(1′:8′*naphthylene*)-cyclo*pentadienone* (I: R=R′=*p*-tol).—Acenaphthenequinone (9 g.) and *sym*-di-*p*-tolylacetone (15 g.) in ethyl alcohol (75 c.c.) were heated on a water-bath with alcoholic potash (2 c.c., 1 : 4). After half an hour the product separated in shining dark violet crystals. It was washed with spirit and crystallised from toluene, m.p. 225°, yield 6 g. (Found: C, 90.37; H, 5.49. $C_{29}H_{20}O$ requires C, 90.62; H, 5.2 per cent).

11 : 12-*Dihydro*-10 : 13-*di*-p-*tolyl*-11 : 12-cyclo*pentenofluoranthene*-11 : 12-*dicarboxylic Anhydride* (III: R=R′=*p*-tol).—2 : 5-Di-*p*-tolyl-3 : 4-(1′ : 8′-naphthylene)-*cyclo*pentadienone (I : R=R′=*p*-tol) (5 g.) and the anhydride of Δ^1-*cyclo*pentene-1 : 2-dicarboxylic acid (2 g.) were refluxed in xylene (20 c.c.), as described before. The adduct was crystallised from a large volume of toluene in needles, m.p. 240° (decomp.), yield 1.8 g. (Found: C, 84.54; H, 5.21. $C_{35}H_{26}O_3$ requires C, 85.02; H, 5.26 per cent).

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VOLUMETRIC ESTIMATION OF SILVER IN COPPER—SILVER MIXTURES CONTAINING MORE THAN 50% COPPER BY VOLHARD'S METHOD

By R. P. Shukla and R. P. Bhatnagar

Volumetric estimation of Ag in Cu-Ag mixtures containing more than 50% Cu has been made by first separating the bulk of Cu from the mixture by ion-exchange method and then estimating the whole of silver by Volhard's method.

No convenient method is known for the volumetric estimation of silver in mixtures containing silver and copper, having copper more than 50%. According to Scott ("Standard Methods of Analysis", 1950, p. 824) the titration by Volhard's method cannot be done when copper is over 60%. According to Sutton ("A Systematic Hand Book of Volumetric Analysis", 1935, p. 141) this method of estimating silver can be used in presence of copper below 70%. Vogel ("A Text Book of Quantitative Inorganic Analysis", 1951, p. 256) states that copper does not interfere provided that it does not form more than 40% of the alloy.

Treadwell and Hall ("Analytical Chemistry", 1935, p. 652) have recommended a procedure of estimating silver in such mixtures. According to them if more than 50% copper is present, the following procedure should be adopted.

"Precipitate the silver by means of an excess of alkali thiocyanate, filter, wash completely with water, then dissolve the silver thiocyanate in concentrated nitric acid by boiling for an hour. As the sulphuric acid formed will have some influence on the titration, barium nitrate solution is added to precipitate it completely and then titration done to estimate silver". This method therefore requires more than two hours for a single estimation. The main difficulty here is the presence of the excess of copper in the mixture of copper and silver as nitrates. A quick procedure to lessen the percentage of copper is the chief aim in this paper. Hence, the present work has been undertaken to separate the bulk of copper by ion-exchange method and then to ascertain if the estimation can be done by Volhard's method.

The work done by the present authors [*Agra Univ. J. Res.* (*Science*), 1954, **3**, 9] on the effective separation of copper from silver-copper mixtures shows that silver has a preferential exchange on sulphonated coal resin as compared to copper and that a suitable column can be prepared to exchange all the silver present in an aliquot volume of the mixture, leaving just a very small part of the resin for copper exchange. Such a process minimises the presence of copper in the mixture to a negligible extent as far as the interference in the estimation of silver by Volhard's method is concerned. Volhard's method can then be used with the usual efficiency to estimate silver, after it has been eluted from the column completely. As has been experienced by us, the method is quick and does not require much skill, if once a suitable column length, its break through capacity, flow rate, etc. are found out.

EXPERIMENTAL

Resin-sulphonated coal was prepared by the method adopted by Bafna, Pai and Shah (*Curr. Sci.*, 1951, **20**, 233).

The resin was used in a column, prepared out of a 50. c.c. burette having a glass wool plug at the bottom and about 1.0 c.c. thick layer of fine sand above it. Preliminary experiments were conducted to find out the break through capacity of the column, and a suitable length was found out for the proper working. In our case, a column of 15 cm. in length and of cross-section of 1.0 sq. cm. was used. Each time a definite volume of the mixture was used in which the amount of silver was within the limits of break through capacity of the column. This ensured the complete exchange of silver present in a known volume of the solution meant for silver estimation. The resin was used in the hydrogen cycle. The column in the process retained all the silver ions present, leaving only a part of the space for copper exchange. The column was then washed with ion-free water so as to remove any adhering copper ions. The resin was regenerated with 6.0% HNO_3. The eluted solution contained all the silver ions with only negligible number of copper ions, even when silver was only 5% and copper 95% by weight in the mixture. Hence, it was possible to estimate silver by Volhard's method in the eluted silver solution. We, proceeding in this manner, were able to estimate silver by Volhard's method in solutions containing only 5% silver and the rest, copper. Our results are shown in Table I.

TABLE I

Resin-sulphonated coal. Column length = 15.0 cm. Column cross-section = 1.0 sq. cm. Flow rate = 5.0 ml./min. Titrant conc. = 0.1*N*-KCNS. Total column capacity = 4.25 m.e. of $AgNO_3$.

% Cu in mixture.	Calc. Ag.	*Ag found by Volhard's method.	% Error.	% Cu in mixture.	Calc. Ag.	*Ag found by Volhard's method.	%Error.
37.02	0.10788 g.	0.10788 g.	0.00	70.00	0.02157 g.	0.02157 g.	0.00
46.60	0.04315	0.04315	0.00	74.60	0.01795	0.01789	0.36
54.40	0.03592	0.03613	0.60	80.00	0.01348	0.01348	0.00
59.30	0.03077	0.03071	0.14	84.01	0.01079	0.01079	0.00
64.50	0.02697	0.02697	0.00	98.32	0.00427	0.00421	0.15

* After applying ion-exchange method.

Thus, it will be seen that by the method of exchange chromatography all the disadvantages of the previous methods are eliminated and still the accuracy is maintained within ±0.5%. Further comment is necessary on Sutton's method (*loc. cit.*) of estimation. To avoid sulphuric acid, he has suggested that it may be precipitated by the addition of barium nitrate and the barium sulphate need not be filtered. But our experience shows that if barium sulphate is not filtered and washed several times with water, the results become a little low, due to adsorption of some of the silver ions by barium sulphate.

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HYDROXYFLUOBERYLLATES. PART III. HYDROXYFLUOBERYLLATES OF COPPER, ZINC, CADMIUM, NICKEL, MANGANESE, MAGNESIUM, COBALT AND IRON

By Grihapati Mitra

The hydroxyfluoberyllate of copper, magnesium, zinc, cadmium, manganese, iron, cobalt and nickel have been prepared and their properties have been described. The compounds crystallise with varying number of water molecules, e.g. 5, 4, 3, 2 and 1. The chemical composition of these compounds is analogous with the corresponding sulphates. The solubilities of these salts are, however, by far greater than the corresponding sulphate or fluoberyllate. Some of these compounds are moreover deliquescent in nature. Nickel hydroxyfluoberyllate hexahydrate has been proved to be isomorphous with nickel sulphate hexahydrate.

Hydroxyfluoberyllates of the alkali metals and some insoluble or sparingly soluble hydroxyfluoberyllates have been described previously by the author (this *Journal*, 1955, **32**, 241, 246). The hydroxyfluoberyllates of the copper-magnesium group of metals are now described. These hydroxyfluoberyllates are highly soluble in water and possess water of crystallisation. The isolation and chemical formulae of these salts prove further that the hydroxyfluoberyllate ion is a quite stable one under the normal conditions and exhibits strong resemblance with the sulphate group.

Experimental

Fluorine in these compounds was estimated as lead chlorofluoride or as calcium fluoride. The other constituents were determined by the standard methods.

Methods of Preparation.—Three general methods were followed for the preparation of these compounds.

(1). A weighed quantity of the carbonate or the freshly precipitated hydroxide of the metal was taken in a platinum basin and dissolved in the minimum quantity of 15% hydrofluoric acid. A slight excess of the equimolecular amount of freshly precipitated beryllium hydroxide was then added to it, and the basin heated on a water-bath; hydrofluoric acid (10%) was added to it little at a time. The addition of hydrofluoric acid was stopped when the solution became just turbid due to the presence of traces of undissolved beryllium hydroxide. The solution was filtered and the filtrate kept in a vacuum desiccator over sulphuric acid at 25° to 35°.

(2). A saturated solution of the nitrite of the metal, obtained by the double decomposition between the sulphate of the metal and barium nitrite, was added to a saturated solution of ammonium hydroxyfluoberyllate. The solution was allowed to crystallise in a vacuum desiccator at the ordinary temperature.

(3). To a concentrated solution of silver hydroxyfluoberyllate a saturated solution containing the requisite amount of the metallic chloride was added. The white

precipitate formed was filtered and the solution was allowed to crystallise in a vacuum desiccator. The crystals obtained after a few days were washed with 60% alcohol and dried by pressing in the folds of a filter paper or in a desiccator.

The first method is by far the best and easiest one. The following compounds were isolated as a result of the present investigation.

Copper hydroxyfluoberyllate pentahydrate was obtained by the first method. The crystals obtained by the second method were always contaminated with some amount of basic salts. (Found : Cu, 26.85 ; F, 23.92 ; Be, 3.66. $CuBeF_3OH.5H_2O$ requires Cu, 26.86 ; F, 24.11 ; Be, 3.81 per cent).

The transparent blue crystals are highly soluble in water and in 80% alcohol ; in latter solvent copper fluoberyllate is practically insoluble. These crystals are perfectly stable. On long exposure to atmospheric conditions a greenish crust is formed due to the formation of the basic salts. When finely powdered crystals of pentahydrated copper hydroxyfluoberyllate are kept over sulphuric acid in a vacuum desiccator for weeks, they lose water to form a monohydrate. (Found : Loss in wt., 30.91%. $CuBeF_3OH.H_2O$ requires loss in wt., 30.45%). At 100° copper hydroxyfluoberyllate becomes green, forming anhydrous salt.

Magnesium Hydroxyfluoberyllate Monohydrate.—The corresponding fluoberyllate salt is not definitely, known. Recently, its existence has been suggested by Perfect (*Proc. Penn. Acad. Sci.*, 1952, **25**, 54). The phase diagram study of the system BeF_2-MgF could not reveal the existence of magnesium fluoberyllate (Venturello, *Atti Accad. Sci. Torino*, 1941, **61**, 556). Hydroxyfluoride complexes are from certain viewpoints more stable than the corresponding fluoride complexes, and isolation of the monohydrated magnesium hydroxyfluoberyllate confirms the above view.

For the preparation of this salt the second method was applied. A few drops of amyl alcohol was, however, added in order to suppress the secondary dissociation. The resulting solution was allowed to concentrate slowly at a low temperature (below 10°). After a week it was filtered and to the filtrate was added an equal volume of alcohol. The solution, thus obtained, was again allowed to crystallise in a vacuum desiccator inside a refrigerator. White microscopic crystals appeared after two days. (Found : Mg, 19.00 ; F, 45.49 ; Be, 6.92. $MgBeF_3OH.H_2O$ requires Mg, 19.39 ; F, 45.45 ; Be, 7.19 per cent).

The substance on heating to 100° lost 14.28% of its weight. H_2O calculated for the monohydrated salt is 14.37%. The heptahydrated and the anhydrous salts could not be isolated. Magnesium hydroxyfluoberyllate is deliquescent in nature.

Zinc hydroxyfluoberyllate heptahydrate was prepared by the first method. The second method also furnished this product, but first two crops should be rejected in this case as they always contained some zinc ammonium hydroxyfluoberyllate as an impurity. (Found : Zn, 23.68 ; F, 20.92 ; Be, 3.12. $ZnBeF_3OH.7H_2O$ requires Zn, 23.81 ; F, 20.76 ; Be, 3.28 per cent).

When this salt was heated to a constant weight at 50°, it changed to the hexahydrated salt. (Found : Loss in wt., 6.72%. $ZnBeF_3OH.6H_2O$ requires loss in wt, 6.56%).

This hexahydrated salt is also obtained when a solution of the heptahydrated zinc hydroxyfluoberyilate is allowed to crystallise on a water-bath. The other hydrated salts could not be isolated. In the case of the sulphate also, the penta-, tetra- and tri-hydrated salts, if they exist at all, are not stable under the ordinary conditions. When the hexahydrated zinc hydroxyfluoberyllate is heated to a constant weight nearly at 200°, the monohydrated salt is formed. (Found : Loss in wt., 39.99%. $ZnBeF_3OH.\ H_2O$ requires loss in wt., 39.3%). The monohydrated salt is appreciably less soluble than the two other hydrated salts.

Cadmium hydroxyfluoberyllate 8/3 *hydrate* was prepared by the first as well as by the second method. This substance is very higroscopic and highly soluble in water and in 60% alcohol. (Found : Cd, 45.97 ; F, 23.39. $CdBeF_3OH.\ 8/3\ H_2O$ requires Cd, 46.15 ; F, 23.41 per cent).

Manganese hydroxyfluoberyllate tetrahydrate is interesting because the magnesium fluoberyllates have not yet been isolated. This salt was prepared by the second method. (Found : Mn, 25.99 ; F, 26.88; Be, 4.11. $MnBeF_3OH.\ 4H_2O$ requires Mn, 26.16; F 27.14; Be, 4.29 per cent).

This salt is also highly soluble in water and is slightly deliquescent. When heated to a constant weight at 85°, it was found to change into the monohydrated salt. (Found : F, 36.52. $MnBeF_3OH.\ H_2O$ requires F, 36.55 per cent).

Ferrous hydroxyfluoberyllate heptahydrate was prepared by the first method. Iron in ferrous hydroxyfluoberyllate shows a marked tendency for absorbing oxygen from air and to change into the ferric state. During the preparation of this compound a few scraps of reduced iron were therefore taken in the platinum basin. The hydrogen liberated by the action of the acid on the metal prevented the oxidation. Alternatively, the reaction may be carried out in an inert atmosphere. The reaction between the ferrous nitrite and ammonium hydroxyfluoberyllate affords a mixture of basic salts, ferrous hydroxyfluoberyllate and possibly ferric hydroxyfluoberyllate. (Found : F, 21.72 ; Fe, 20.68 ; Be, 3.19. $FeBeF_3OH.\ 7\ H_2O$ requires F, 21.51 ; Fe, 21.12 ; Be, 3.40 per cent).

Ferrous hydroxyfluoberyllate is almost colorless, and when kept over sulphuric acid in a desiccator it loses nearly three molecules of water, yielding the tetrahydrated salt.

Cobalt hydroxyfluoberyllate heptahydrate was prepared by the first and the third methods. The solution was allowed to crystallise in a refrigerator. (Found : Co, 21.61 ; F, 21.00 ; Be, 3.27. $CoBeF_3OH.\ 7H_2O$ requires Co, 21.85 ; F, 21.26 ; Be, 3.36 per cent).

When the solution was allowed to crystallise on the water-bath, the hexahydrated compound was obtained. (Found : F, 22.67., $CoBeF_3OH.\ 6\ H_2O$ requires F, 22.80 per cent).

The rose-red crystals are converted into the trihydrated salt when kept in a vacuum desiccator over sulphuric acid. (Found : Loss in wt., 21.40%. $CoBeF_3OH.\ 3\ H_2O$ requires loss in wt., 21.62%).

On heating the hexahydrated salt to a constant weight at 80°, the dihydrated salt was obtained as a dusty red powder. (Found : Loss in wt., 29.73%. $CoBeF_3OH.2\ H_2O$ requires loss in wt., 28.82%).

The cobaltic hydroxyfluoberyllate could not be prepared but its ammines have been isolated.

Nickel Hydroxyfluoberyllate Heptahydrate.—When the solution obtained by the first method was allowed to crystallise at a temperature below 20° beautiful green monoclinic crystals of nickel hydroxyfluoberyllate heptahydrate were obtained. (Found : Ni, 21.70 ; F, 21.23 ; Be, 3.32. $NiBeF_3OH.7\ H_2O$ requires Ni, 21.92 ; F, 21.28 ; Be, 3.37 per cent).

If during the process of crystallisation the temperature of the solution goes above 30°, the hexahydrated salt is obtained. (Found : Ni, 23.32 ; F, 22.68 ; Be, 3.58. $NiBeF_3OH.\ 6\ H_2O$ requires Ni, 23.49 ; F, 22.82 ; Be, 3.61 per cent).

The hydroxyfluoberyllate of nickel is highly soluble in water. At 30° 100 c. c. of the saturated solution contains 39.5 g. of nickel fluoberyllate, while the same amount of a saturated solution of nickel hydroxyfluoberyllate at the same temperature contains 69.8 g. of nickel hydroxyfluoberyllate.

The other hydrated salts of nickel hydroxyfluoberyllate could not be isolated. In the case of sulphate also, the penta-, tetra-, tri- and di-hydrated salts are metastable (Chretien and Rohmer, *Compt. rend.*, 1934, **193**, 92). The crystalline overgrowth of the nickel hydroxyfluoberyllate on a crystal of nickel sulphate was observed. These two salts are therefore isomorphous. Similar observation has already been made in connection with the potassium and barium salts by X-ray analysis.

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A COMPARATIVE STUDY ON SOME CHEMICAL CHARACTERISTICS OF JUTE AND *HIBISCUS* FIBRES

By W. G. Macmillan, A. B. Sen Gupta and A. Roy

A comparative study has been made on the chemical composition as well as on the characteristic functional groups of jute and fibres of the *Hibiscus* group, namely Mesta, Bimli and Kenaf, with a view to differentiating these fibres on the basis of chemical properties. From analyses of a number of different samples it is confirmed that the yield of lignin or holocellulose, obtained from jute, is significantly different from those of other allied fibres. Although a wide variation is observed in the carboxyl existing in different states, *i.e.* free and combined, in jute and *Hibiscus* fibres, no definite conclusion can be drawn from the results obtained. The acetyl content, total acidity and the methoxyl associated with the carbohydrate fraction of jute are significantly lower than those of fibres of the *Hibiscus* group, and these values may be taken as additional criteria for differentiating jute and other allied fibres. Further, since the acetyl content and the total acidity of *Corchorus capsularis* fibre (White jute) are considerably high compared with those obtained from *Corchorus olitorius* fibre (Tossa or Daisee jute), it seems possible that from the variations in these values the two botanical species of jute fibre can be differentiated from each other.

A number of bast fibres, closely allied to jute which belongs to *Corchorus* species, can be successfully processed on jute mill machinery. The most common of these substitute fibres are derived from the *Hibiscus* plant, usually from the species known as *H. cannabinus*, and are described by a variety of different names but, in India, are usually known as either Mesta or Bimli and in other countries as Kenaf. The quality of *Hibiscus* fibres, so far as the spinning property is concerned, varies similar to that of jute, but generally speaking, these fibres are coarser and more brittle than jute and, as a result, are less suitable for the spinning of fine yarns.

The principal characteristic feature of jute and the *Hibiscus* fibres is, that although cellulose forms the main structural component, it does not occur in the pure state but is associated predominantly with lignin and hemicelluloses. The chemical compositions as well as the physical and chemical properties of these fibres are so akin to each other that it is extremely difficult to differentiate them. Since the *Hibiscus* fibres are coarser and stiffer than jute, differentiation of these fibres is usually made by visual examination and by feel. The present work was initiated with the object of differentiating these fibres not only on the basis of chemical composition but also on the characteristic functional groups which until recently have been considered of little importance.

It has been reported by Powrie and Speakman (*J. Text. Inst.*, 1943, **34**, T77) and more recently by Das, Mitra and Wareham (*ibid.*, 1951, **42**, T181) that jute contains a higher percentage of lignin in comparison with Mesta and Bimli while the variation in the other main constituents, *i.e.*, α-cellulose, pentosan calculated as xylan, polyuronide and hexosan, of jute from those of other allied bast fibres is of such a small order that it can be regarded as insignificant. The procedure employed by Das *et al.* (*loc.cit.*) for the determination of lignin is not very accurate, since the lower yield obtained by this method has been found to be due to a partial solubility of lignin in the reagent used

for its isolation (Sen Gupta and Callow, *ibid.*, 1949, **40**, T650; Macmillan, Sen Gupta and Roy, *ibid.*, 1952, **43**, T103). A more correct value, however, is expected to be obtained by the method suggested by Sen Gupta and Callow (*loc.cit.*). It was considered of importance therefore to re-examine the lignin content of these fibres with a more accurate procedure in order to ascertain whether the difference between the values of lignin in jute and other allied fibres was really significant.

In addition to the major constituents, jute fibre contains a number of characteristic functional groups, namely carboxyl, acetyl and methoxyl, which are generally regarded as of minor importance, and until recently, have received no serious attention. More recent investigations (Bhattacharjee and Callow, *ibid.*, 1952, **43**, T53; Macmillan and Sen Gupta, this *Journal*, 1952, **29**, 737) have shown that the acidity of jute is due to both uronic carboxyl and acetyl groups. Uronic carboxyl groups have been found to exist in three different states, a small portion (3 m.e./100 g., approx.) being in the free state and the major portion in the combined form, of which a part is occupied with cations (9 m.e./100 g.) and the rest (12 m.e./100 g.) in the ester combination with the hydroxyl group of lignin (Sarkar, Chatterjee and Mazumdar, *J. Text. Inst.*, 1947, **38**, T318). The acetyl, which amounts to approximately 3.5% on jute, occurs in combination with the hydroxyl groups, mainly, if not entirely, associated with the carbohydrate fraction (Macmillan and Sen Gupta, *loc.cit.*) and is easily hydrolysed by the action of dilute caustic soda solution at room temperature. It has been demonstrated that of the methoxyl groups in jute, the major portion is associated with the lignin residue, the remainder being attached to the hemicellulosic fraction (Sen Gupta and Callow, *J. Text. Inst.*, 1951, **42**, T382), possibly the uronic acid residue (Sarkar, Mazumdar and Pal, *Textile Res. J.* 1952, **22**, 529). Although a considerable amount of work has been carried out on the functional groups in jute, no data appear to be available on the occurrence of these groups in other allied fibres, and there is a possibility that such groups will vary not only in amounts but also in proportions, existing in combination with different fibre components. In the present investigation therefore, attention was particularly directed towards the relative proportions as well as the mode of occurrence of these groups with a view to obtaining some additional evidence for differentiating jute more positively from the fibres of the *Hibiscus* group.

Experimental

Three different samples of jute, three of Mesta, two of Bimli and one of Kenaf were employed in the present investigation. The White and Tossa varieties of fibre, belonging to *C. capsularis* and *C. olitorius* species respectively, were of good quality jute obtained from Pakistan, while the samples of Daisee jute (also *C. olitorius*) and those of Mesta were procured from different parts of West Bengal; Bimli fibres were obtained from Madras and Kenaf, which was the only sample available, was imported from Australia. Representative samples, obtained from the middle portions of the strands of different fibres, were de-waxed by extracting the materials with a mixture of alcohol-benzene (1 : 2), washed successively with alcohol and water, and air-dried. Experiments were conducted with the air-dried samples and the analytical results expressed on the oven-dry (at 105°) weight of the fibres.

Lignin was determined by the 72% sulphuric acid procedure, as modified by Sen Gupta and Callow (*J. Text. Inst.*, 1949, **40**, T650).

For isolation of the holocellulose fraction, the fibre sample was subjected to two successive treatments with hot (98°) sodium chlorite solution (0.7%, using a liquor ratio 50:1) maintained at p_H 4, the duration of each treatment being 2 hours, followed by treatment with 2% sodium bisulphite.

The free carboxyl and that occupied with cations were determined by the procedure suggested by Sarkar, Chatterjee and Mazumdar (*loc. cit.*); the uronic carboxyl occurring as ester was obtained from the measure of the increased acidity of the fibre after a hydrolytic treatment with caustic soda (Macmillan and Sen Gupta, *loc.cit.*).

The acetyl content was ascertained by hydrolysing the material with caustic soda and then measuring the steam-volatile acetic acid by the procedure followed by Macmillan and Sen Gupta (*loc.cit.*).

The total acidity (*i.e.* both due to uronic and acetic acid residues) was ascertained directly by allowing the fibre to react with an excess of caustic soda and estimating the amount of alkali required for neutralisation (Macmillan and Sen Gupta, *loc.cit.*).

The methoxyl content was determined by a modified Zeisel method, as previously used by Sen Gupta and Callow (*loc. cit.*).

The values of lignin, uronic carboxyl existing in different states, acetyl and the total acidity of the various samples analysed are recorded in Table I.

TABLE I*

Lignin, acetyl and uronic acid contents, and total acidity of jute and Hibiscus *fibres.*

Material.	% Lignin.	Uronic carboxyl (m.e./100 g.). Free.	Occupied with cation.	Occurred as ester.	%Acetyl.	Total acidity (m.e./100 g.).
Jute (White)	14.29	2.03	8.12	10.64	3.80	113.1
,, (Tossa)	13.90	...	...	...	3.17	100.0
,, (Daisee)	12.80	...	...	...	3.25	101.7
Mesta (Sample 1)	9.49	1.63	5.52	12.09	5.21	143.2
,, (Sample 2)	10.47	...	...	...	5.16	139.2
,, (Sample 3)	9.70	...	...	...	5.09	138.8
Bimli (Sample 1)	9.88	1.69	6.91	11.86	5.09	138.7
,, (Sample 2)	10.07	...	...	...	5.26	146.3
Kenaf	10.80	2.11	15.44	9.25	4.46	127.8

* Results are expressed on oven-dry de-waxed fibre.

DISCUSSION

In addition to the results obtained in the present investigation, analyses of various samples of jute carried out in the Ijmari laboratories over a period show that the lignin content of jute generally varies from 12 to 14.5%, as determined by the modified 72% sulphuric acid procedure, some difference in the values being noted on changing the method of estimation. It is seen from the results in Table I that the lignin content of the other allied bast fibres studied lies within the range of 9.5 to 10.8%. Jute therefore

appears to contain a higher percentage of lignin, compared with fibres of the *Hibiscus* group, and the difference in the values for jute and those of the other bast fibres examined can be considered as significant.

The uronic acid content of jute, Mesta and Bimli is approximately the same, while that of Kenaf is appreciabely higher. A wide variation has been observed in the values of carboxyl occurring in different states and no definite conclusion can, however, be drawn from the results obtained.

Besides the results recorded in Table I, various samples of White, Tossa and Daisee jute, analysed in these laboratories, demonstrate that the acetyl content and the total acidity of jute are always within the limit of 3.1 to 3.8% and 100 to 114 m.e./100 g. respectively, the corresponding values for *Hibiscus* fibres being 4.5 to 5.2% and 128 to 146 m.e./100 g. Both the acetyl content as well as the total acidity of the other allied bast fibres are significantly higher than those obtained from jute, and these values may therefore be taken as additional criteria for differentiating jute from fibres of the *Hibiscus* group. The difference in the total acidity of these fibres, however, appears to be mainly due to variation in the acetyl content of the individual fibre samples. Further, the values of acetyl content and total acidity of White jute (*C. capsularis*) have been found to vary from 3.6 to 3.8% and 110 to 114 m.e./100 g. respectively, while those obtained from other variety of jute (*C. olitorius*) always lie within the range of 3.1 to 3.25% and 100 to 102 m.e./100 g. It seems possible therefore that from the variations of these values jute fibre belonging to two botanical species can be differentiated from each other.

Holocellulose, isolated from any of the fibres by one treatment with sodium chlorite, as recommended by Chattopadhyay and Sarkar (*Proc. Nat. Inst. Sci., India*, 1946, **12**, 23), was found to be contaminated with 1.8 to 2.0% lignin (on the weight of the holocellulose). Two such treatments, however, effect a considerable reduction in the lignin content, as shown in Table II, without any undue loss in the hemicellulose content, as is evident from the summation of lignin and holocellulose of the fibre approaching very near to 100 (Tables I and II). Any attempt to reduce the lignin content still further, by increasing the number of treatments, resulted in a marked elimination of hemicellulosic constituents. In the present work therefore the holocellulose content was determined by two treatments of acidic sodium chlorite.

The methoxyl content was estimated on individual fibres as well as on lignin and holocellulose, isolated from the respective samples. From the value of methoxyl of the isolated lignin and the lignin content of the corresponding fibre, the amount of methoxyl associated with the lignin *in situ* (expressed as a per cent on fibre) was obtained. A theoretical value of the methoxyl associated with the carbohydrate fraction was then calculated from the difference of the methoxyl content of the fibre and that of the lignin *in situ*. This value, however, will tend to be higher if lignin loses some of its methoxyl groups during the process of isolation (Dorée, "The Methods of Cellulose Chemistry", 1947, p. 366). In order to obtain the methoxyl attached to carbohydrate from a direct estimation of holocellulose, a correction was applied for the presence of residual lignin, an

assumption being made that the methoxyl content of the residual lignin was identical with that of the lignin isolated from the untreated fibre. This value is also expected to be deviated from the correct methoxyl content of carbohydrate by a number of factors. For example, a positive error is likely to be involved owing to the possibility of holocellulose being contaminated with the lignin degradation products containing methoxyl (Sen Gupta and Callow, *J. Text. Inst.*, 1951, **42**, T382) and a negative error if a partial demethylation of either the residual lignin or the carbohydrate fraction or both, occurs during delignification. Since it is not known which one of the values, *i.e.* the calculated and that obtained by the direct estimation of holocellulose, will afford a more correct indication of the actual methoxyl content of the carbohydrate fraction, both values of the *Hibiscus* fibres have been compared with those obtained from jute. A summary of the results is shown in Table II.

TABLE II*

Holocellulose content, and associated methoxyl in lignin and carbohydrate fractions of jute and Hibiscus *fibres.*

Material.	Holocellulose.	Lignin in holocellulose.	%OMe associated with lignin on		%OMe associated with carbohydrate.	
			** lignin.	fibre.	Calc.	Found
Jute (White)	85.25%	0.54%	19.25	2.75	0.89	0.95
Mesta (Sample 1)	91.07	0.54	21.19	2.01	1 66	1.27
Bimli (Sample 1)	90.67	0.50	19.03	1.88	1.48	1.34
Kenaf	89.75	0.55	18.83	2.03	1.36	1.26

* Results are expressed on oven-dry de-waxed fibre.

** Results are expressed on oven-dry lignin.

As expected from variations in the lignin contents of jute and other allied fibres, the results in Table II show that the difference in the yield of holocellulose of these fibres is also significant. The methoxyl content of lignin (as a per cent on lignin), isolated from different fibres, is more or less the same. The observed variations in the values of methoxyl in lignin (per cent on fibre) are obviously due to difference in the lignin content of the individual fibres. Analyses of various samples of jute reveal that methoxyl in carbohydrate varies within the limit of 0.85 to 0.95% while in the case of *Hibiscus* fibres the values have always been found above 1.25%. The methoxyl associated with the carbohydrate fraction of jute therefore seems to be appreciably lower than that of allied fibres, the difference being more marked in calculated values.

It appears possible from the results † described that jute can be differentiated from fibres of the *Hibiscus* group by the variation in the values of lignin or holocellulose, acetyl, total acidity and the methoxyl associated with the carbohydrate fraction.

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STUDIES IN INDIGOID DYES. PART XVII. THIOINDIGOID DYES DERIVED FROM DIPHENYL ETHER DISULPHONIC ACID

By Paresh Chandra Dutta and Dasrath Mandal

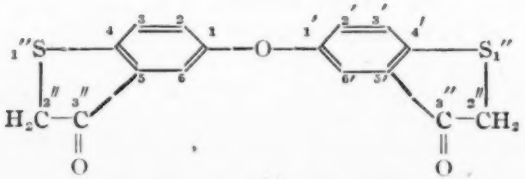
4 : 5-4′ : 5′-Diphenyl-*bis*-(3″-hydroxy-1″-thiophene)-ether (I), prepared from diphenyl ether-4 : 4′-disulphonic acid, has been condensed with various *o*-diketones, and the corresponding *bis*-thioindigoid dyes have been obtained with a view to studying colour and its relation to chemical constitution.

After having unsuccessful attempts to prepare dithioindigoid dyes from diphenyl-4 : 4′-disulphonic acid (this *Journal*, 1955, **32**, 339) and naphthalene-2:7-disulphonic acid (*ibid.*, 1955, **32**, 423), it has been possible to prepare such dyes from diphenylmethane-4 : 4′-disulphonic acid (*ibid.*, 1955, **32**, 497). These dyes, although dithioindigoids and as such expected to be of much deeper in colour, have not been found so deep. The deficiency in depth of colour has been ascribed to the presence of the insulating group $-CH_2-$ in between the two thioindigoid chromphores, thus breaking the conjugated system of the whole molecule in two parts, producing the colour effect by only the duplication or addition of the two monothioindigoid parts on either side. The present investigation is an attempt to study further such dithioindigoid dyes with respect to their colour and chemical constitution, and it deals with dyes derived from diphenyl ether disulphonic acid so that in place of the methylene bridge therein, an ether linkage (-O-) is present in the present series.

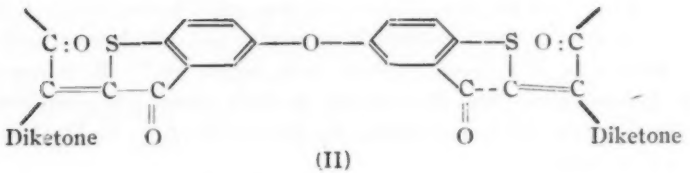
As the ether linkage in these compounds should also act as an insulator, like the methylene group, breaking the conjugated system into fragments, something very different from the previous observation was not expected. This assumption has been realised on comparing the colour of these two series of dyes, excepting that the divalent oxygen appears to have a slightly greater chromophoric effect than the methylene group, as the dyes described herein have a slightly deeper shade.

For preparing these dyes, diphenyl ether has been converted successively into its disulphonic acid (*Annalen*, 1863, **125**, 329; 1871, **159**, 204), disulphochloride, dimercaptan, dithioglycollic acid and the latter cyclised to dithioindoxyl. This dithioindoxyl has been condensed with various *o* diketones, and thus *bis*-thioindigoid dyes have been obtained.

The positions of the sulphonic acid groups in the diphenyl ether disulphonic acid having been known (Suter, *J. Amer. Chem. Soc.*, 1931, **53**, 1115), the structures of the dithioindoxyl (I) and the thioindigoid dyes (II), obtained from it, may be represented by the following formulae :



(I)



(II)

EXPERIMENTAL

Diphenyl ether-4 : 4′-disulphochloride was prepared by heating a mixture of diphenyl ether potassium disulphonate (35 g.) and PCl_5 (50 g.) on a water-bath for 2 hours when a semi-fluid mass was obtained. This was decomposed by ice and left overnight. The residue, after washing and drying, was crystallised from chloroform in small cubes, m.p. 131°. (Found : C, 39.12 ; H, 2.23. $C_{12}H_8O_5Cl_2S_2$ requires C, 39.23 ; H, 2.18 per cent).

Diphenyl Ether-4 : 4′-dimercaptan.—The above disulphochloride (whole quantity) was reduced with tin and HCl for 12 hours when a soft yellowish mass was obtained. This was filtered, washed first with HCl (conc.) and then with water. The residue was then extracted with benzene, the extract dried with calcium chloride, filtered and the benzene distilled off. The mercaptan, separating as shining yellow flakes, was recrystallised from alcohol, m.p. 103-104°, yield 15 g. (Found : C, 61.47 ; H, 4.31. $C_{12}H_{10}OS_2$ requires C, 61.53 ; H, 4.27 per cent).

Diphenyl Ether-4 : 4′-dithioglycollic Acid.—The dimercaptan (4.8 g.) was dissolved in dilute caustic soda and to this monochloroacetic acid (4 g.), previously neutralised with caustic soda, was added. The mixture was warmed on a water-bath for an hour, filtered and the filtrate acidified with HCl. The dithioglycollic acid separating as a white voluminous precipitate was crystallised from dilute alcohol as white shining flakes, m.p. 164°, yield 6.2 g. (Found : C, 55.3 ; H, 3.9. $C_{16}H_{14}O_5S_2$ requires C, 54.85 ; H, 4.0 per cent).

4 : 5 4′:5′-*Diphenyl*-bis-(3″-*hydroxy*-1″-*thiophene*)-*ether* was prepared in the same way as 4 : 5-4′ : 5′-diphenyl-*bis*-(3″-hydroxy-1″ thiophene)-methane (*loc. cit.*) from the above diphenyl ether-dithioglycollic acid. The crude dithioindoxyl like the other similar compounds could not be purified on account of its susceptibility to oxidation, and so its acetic acid solution was used for condensation with various *o*-diketones. The thioindoxyl dissolves in dilute caustic soda with a greenish colour, but does not yield any precipitate of the *bis*-compound with potassium ferricyanide.

4 : 5-4′ : 5′-*Diphenyl*-bis-*thiopheno-ether*-3 : 3-bis-*indoi-indigo* (IIa) was prepared by mixing the separate solutions of isatin and the above thioindoxyl in acetic acid and boiling the mixture for half an hour with the addition of HCl (conc., 0.5 c.c.). The violet-red precipitate obtained was filtered hot, washed with acetic acid and alcohol and crystallised from nitrobenzene as a violet-red crystalline mass, m.p. above 300°. It dissolves in alkaline hydrosulphite with a yellow colour and dyes cotton in pinkish violet shade. In H_2SO_4 (conc.) it dissolves with a greenish brown colour. (Found : C, 66.7 ; H, 3.3. $C_{32}H_{16}O_5N_2S_2$ requires C, 67.13 ; H, 2.8 per cent).

4:5-4′:5′-*Diphenyl*-bis-*thiopheno-ether*-2:2-bis-*acenaphthylene-indigo* (IIb) was prepared, as described above, from acenaphthenequinone and dithioindoxyl and crystallised from nitrobenzene as tiny, pink needles, m.p. above 300°. It is not much soluble in alkaline hydrosulphite and dyes cotton in pink shade. It dissolves in H_2SO_4 (conc.) with a green colour. (Found: C, 74.32; H, 3.3. $C_{40}H_{18}O_5S_2$ requires C, 74.76; H, 2.8 per cent).

4 : 5-4′ : 5′-*Diphenyl*-bis-*thiopheno-ether*-9 : 9-bis-*phenanthrene-indigo* (IIc) was prepared, as already described, from phenanthrenequinone and dithioindoxyl and obtained as a dark chocolate crystalline mass from nitrobenzene, m.p. above 300°. It dissolves in H_2SO_4 (conc.) with a brown colour and dyes cotton from alkaline hydrosulphite in chocolate-brown shade. (Found : C, 75.97; H, 3.25. $C_{44}H_{22}O_5S_2$ requires C, 76.08; H, 3.17 per cent).

4 : 5-4′ : 5′-*Diphenyl*-bis-*thiopheno-ether*-1 : 1-bis-*aceanthrylene-indigo* (IId) was prepared from aceanthraquinone and dithioindoxyl in acetic acid solution, as described above, and crystallised from nitrobenzene as a brownish violet crystalline mass, m.p. above 300°. It dyes cotton from hydrosulphite vat in copper-red shade and dissolves in H_2SO_4 (conc.) with a light green colour. (Found: C, 77.51; H, 3.02. $C_{48}H_{22}O_5S_2$ requires C, 77.62; H, 2.96 per cent).

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ALTERNATING CURRENT ELECTROLYSIS. PART IV. ELECTROLYSIS OF SULPHURIC ACID SOULTIONS WITH COPPER ELECTRODES

By K. M. Joshi

Chemical effects, produced by passing a square-wave type alternating current between copper electrodes in sulphuric acid solution, have been studied. Hydrogen evolution, takes place at both the electrodes but the rate of gas evolution falls rapidly at one of the electrodes at which gas evolution ceases entirely after some time. Copper goes into solution and the electrodes at the end of the experiment are covered with a deposit of copper. The volume of hydrogen evolved diminishes markedly with frequency of alternation and concentration of electrolyte, and increases with current density, temperature and area of electrodes. The rate of gas evolution is proportional to time during initial stages of experiment but falls off with time.

A mechanism depending upon the dissolution of copper during the anodic cycle and deposition of copper and hydrogen evolution during cathodic cycle has been proposed. The fall in the rate of gas evolution is tentatively ascribed to the surface being replaced by electrodeposited copper having entirely different surface characteristics.

The present work is in continuation of the investigation on alternating current electrolysis, using square-wave type A. C. (this *Journal*, 1954, **31**, 278). Copper electrodes are chosen mainly because copper will function as an attackable electrode in sulphuric acid solutions. The effects of frequency, current density, temperature, concentration of electrolyte and duration of electrolysis have been studied with a view to gaining an insight into the mechanism of electrode reactions in alternating current electrolysis.

Experimental

The experimental arrangement was the same as used in the previous investigation (this *Journal*, 1952, **29**, 69). The electrodes were cut from Kahlbaum extra pure electrolytic copper foil. These were sealed into J-shaped glass tubing, lead glass being used for sealing copper into glass. The electrolyte was prepared from G. R. sulphuric acid and standardised against standard NaOH. The electrode gases were collected in gas collecting cups attached to calibrated gas burettes. The analysis of gas mixtures was done by absorbing the gas in alkaline pyrogallol. The gas mixture, comprising only hydrogen and oxygen, on absorption by pyrogallol afforded the volume of oxygen. The residual gas was found to be only hydrogen. In all the experiments there was complete absence of oxygen in the electrode gas.

The electrodes were cleansed with very dilute nitric acid and then washed with plenty of distilled water. Finally, the electrodes were dipped in dilute ammonia solution, and after washing with water, were immediately used for the experiment. This treatment was found to furnish reproducible results.

It was observed during electrolysis that on switching on current, gas evolution took place on both the electrodes, but in a short time, depending on the frequency,

current density etc., one of the electrodes lost its activity of gas evolution gradually, and ultimately gas evolution stopped entirely at this electrode. Although the other electrode continued to evolve gas, but with time, the rate of gas evolution also slowed down. At the end of the experiment, a fine non-adhering deposit of copper was observed on both the electrodes. The electrolyte also became faint blue due to the dissolution of copper at the electrodes.

Table I shows the effect of frequency of alternation on the total volume of hydrogen evolved at each electrode. In this and other tables, the term 'Electrode-I' is applied to any one of the electrodes in an experiment. It does not mean that 'Electrode-I' in all experiments is the same piece of copper used.

TABLE I

Area of electrodes = 4 cm^2. Current = 1 ampere.

Electrolyte : $N/5$-H_2SO_4. Ampere hours passed = 1.5.			Electrolyte : $N/20$-H_2SO_4. Ampere hours passed = 1.0.		
Frequency (per sec.).	Volume of H_2 by Electrode-I.	Electrode-II.	Frequency (per sec.).	Volume of H_2 by Electrode-I.	Electrode-II.
5	39.6 c.c.	0.5 c.c.	3	48.4 c.c.	40.0 c.c.
10	15.8	0.2	5	35.6	34.2
20	5.5	0.2	10	23.0	13.5
30	5.3	0.2	20	12.4	4.1
40	4.0	0.2	30	9.3	7.0
			40	8.3	4.7

Table II records the effect of current density on the volume of gas evolved at each electrode. It is to be observed here that the amounts of gas evolved at the two electrodes are not the same, and in different experiments the ratio of volume of gas evolved at electrode-I/volume of gas evolved at electrode-II is not identical. Table III shows the effect of time on the volume of gas evolved at an electrode.

TABLE II

Electrolyte : $N/20$-H_2SO_4. Frequency = 10 per second. Ampere hours passed = 1
Area of electrodes = 4 cm^2.

Current density.	Volume of H_2. Electrode-I.	Electrode-II.
125.0 ma/sq.cm.	9.0 c.c.	5.0 c.c.
187.5	19.9	14.6
250.0	23.0	20.5
312.5	31.2	26.4
375.0	35.0	29.3
437.5	40.0	33.8

TABLE III

Electrolyte : $N/20$-H_2SO_4. Area of electrodes = 4 sq. cm. Current = 1 amp.

Frequency = 10 per second.				Frequency = 20 per second.			
Time.	Vol. of H_2.	Time.	Vol. of H_2.	Time.	Vol. of H_2.	Time.	Vol. of H_2.
2 min.	0.8 c.c	30 min.	7.7 c.c.	5 min.	1.3 c.c.	37 min.	7.8 c.c
5	1.7	35	9.2	10	2.2	44	9.3
10	2.6	40	10.5	15	3.2	50	10.4
15	4.2	45	11.9	20	4.2	60	12.6
20	5.4	50	13.5	25	5.3		
25	6.4	60	16.3	30	6 4		

Table IV shows the influence of concentration of electrolyte on the volume of gas evolved at each electrode and Table V, the effect of temperature on the volume of hydrogen evolved at each electrode.

TABLE IV

Area of electrodes = 4 cm^2. Current = 1 amp. Duration of electrolysis = 1 hr.

Conc. of H_2SO_4 ...		$N/2$	$N/4$	$N/8$	$N/10$	$N/16$	$N/20$	$N/40$
Vol. of H_2 in c.c.	Electrode-I	1.4	5.0	6.2	13.5	16.4	19.8	24.6
	Electrode-II	4.6	6.0	11.0	23.0	25.3	27.2	30.3

TABLE V

Electrolyte : $N/20$-H_2SO_4. Frequency = 10 per sec. Current = 1 amp.
Duration of electrolysis = 60 mins.

Temp. ...		36°	40°	51°	70°	80°
Vol of H_2 in c.c.	Electrode-I	23.0	21.0	24.6	30.8	35.8
	Electrode-II	13.5	18.5	24.0	29.5	34.0

Table VI shows the influence of area of electrode at the same current density on the volume of gas evolved at each electrode.

TABLE VI

Current density = 500 ma./cm^2. Amp. hour passed = 1. Frequency = 10 per sec.
Conc. of $H_2SO_4 = N/20$.

Electrode area (cm^2.) ...		2.0	3.2	4.0	5.2	6.0
Vol. of H_2 in c.c.	Electrode-I	30.3	23.7	13.5	15.0	17.6
	Electrode-II	34.0	30.9	23.0	23.5	20.6

Discussion

The most interesting feature of the present investigation is the totally unsymmetrical behaviour of the electrodes in that one of them continues to function as hydrogen evolving while the other, after showing hydrogen evolving activity for some time, ceases to function as a gas-evolving electrode during the experiment. It has also been observed that if the current is slowly increased, one of the electrodes alone functions as hydrogen-evolving while at the other electrode, the rate of gas evolution decreases rapidly with time. On the other hand, if the current is switched on suddenly, a brief period of gas evolution is observed at the electrode. The gas-evolving electrode, too, gradually loses its gas-evolving activity with time. This phenomenon is more marked in concentrated solutions of sulphuric acid. In very dilute solutions, however, both the electrodes continue to function as hydrogen evolving though the efficiency at the electrodes is never the same.

Another important observation that has been made is that both the electrodes become coated with a non-adherent layer of electrodeposited copper. From the data presented above, it will be seen that the current efficiency of hydrogen evolution falls very rapidly with frequency of alternation, while at the same frequency, the plot of current density against the volume of hydrogen evolved (Table II) is a straight line at higher values of current density. The volume of hydrogen evolved at an electrode is roughly proportional to the time during the initial stages of electrolysis. Lower concentrations of sulphuric acid and higher temperatures favour the evolution of hydrogen. At the same current density, the volume of hydrogen evolved depends on the area of electrodes (Table VI).

When a copper electrode, suspended in a solution of sulphuric acid, is subjected to cathodic and anodic polarisation alternately, the reactions that can take place at the electrode are :

$$\text{During the cathodic cycle: } H^+ + e \longrightarrow H \quad \ldots (1)$$

$$H + H \longrightarrow H_2 \quad \ldots (2)$$

while during the anodic cycle, at lower potentials the metal may go into solution. At higher values of current density, in D. C. electrolysis, copper is known to become passives and evolves oxygen. The latter stage does not seem to occur since oxygen is not found in the electrode gas. Thus, the anodic reactions may be :

$$Cu \longrightarrow Cu^{2+} + 2e \quad \ldots \quad \ldots (3)$$

$$Cu^{2+} + SO_4^{2-} \longrightarrow CuSO_4 \quad \ldots \quad \ldots (4)$$

Copper will therefore dissolve out during the anodic cycle at some favourable spots on the electrode surface, resulting in the formation of copper sulphate at the metal-solution interface, while some of the copper sulphate may diffuse into the bulk of the solution. The amount of copper sulphate in solution being small, it suggests that the anodic dissolution process is reversed to an appreciable extent during the cathodic cycle :

$$Cu^{2+} + 2e \longrightarrow Cu \quad \ldots \quad \ldots (5)$$

or

$$2H + SO_4 \longrightarrow H_2SO_4 \quad \ldots \quad \ldots (6)$$

Thus, electrodeposited copper appears on the electrode during the cathodic cycle. As $[Cu^{2+}]$ concentration in the vicinity of the electrode is depleted, the electrode potential rises and the discharge of $[H^+]$ takes place. Thus, near the end of the cathodic cycle, the electrode becomes a hydrogen-evolving one. At higher values of frequency of alternation, the period of duration of a half cycle is small. During the anodic half cycle, most of the copper dissolved at the electrode remains in the vicinity of the electrode. When this electrode is subjected to cathodic polarisation, most of the dissolved copper is deposited on the electrode as the duration of half cycle being small, very little $[Cu^{2+}]$ will diffuse into the bulk of the solution. Thus, at higher values of frequency, the chemical effects of one impulse are more or less completely reversed during the next half cycle. Hence, the volume of hydrogen evolved diminishes with frequency. Again, at higher current density, we must expect a greater dissolution resulting in a faster rate of diffusion of $[Cu^{2+}]$ into the bulk of solution. Thus, during the cathodic cycle, the depletion in $[Cu^{2+}]$ concentration will be brought about much quicker, resulting in a greater evolution of hydrogen. The effect of temperature can be explained by the same mechanism, as higher temperature will increase the rate of diffusion of $[Cu^{2+}]$ favouring hydrogen evolution.

With the progress of electrolysis, $[Cu^{2+}]$ concentration in the electrolyte will go on increasing as, excepting at higher frequencies, the dissolution and deposition processes are not exactly balanced. This will cause the cathodic behaviour of copper to change altogether as the rate of diffusion of $[Cu^{2+}]$ towards the electrode and the rate of deposition may be comparable ; hence, the cathodic process may entirely be the deposition of copper, resulting in the stoppage of H_2-evolution at the electrodes. Why this condition should be obtained at one of the electrodes much earlier than at the other is a point which needs explanation. This behaviour may be due to (*i*) the covering up of the active centres where either the discharge of $[H^+]$ or combination of H atoms can occur by electrodeposited copper ; (*ii*) the different history of the electrode in that during electrolysis, the first impulse must be opposite in polarity to that at the other electrode. This may possibly determine the behaviour of the electrode during the rest of the experiment. This point has been verified experimentally as follows. Two copper electrodes were subjected to D. C. electrolysis for a short time in $N/10$-H_2SO_4. When electrolysis was in progress, A. C. was switched on and the D. C. was stopped by a mechanical device. It was found that the electrode, which was cathodically polarised in D. C. electrolysis, continued to function as gas-evolving in A. C. electrolysis, while the electrode which was subjected to D.C./anodic polarisation did not show any gas evolution in A. C. electrolysis. It seems therefore that the first impulse during A. C. electrolysis is the determining factor in the behavour of an electrode.

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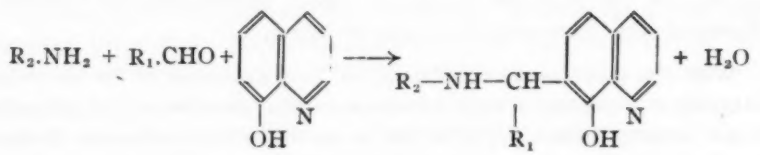
REACTION OF ALDEHYDES AND AMINES WITH 8-QUINOLINOL

By A. B. Sen and M. S. Saxena

Several 7-α-anilino-benzyl-8-quinolinols have been synthesised by a Mannich type of reaction between aldehydes, amines and 8-quinolinol with a view to studying their amoebecidal activity, and as precipitants for metal ions.

An unusually simple Mannich type of reaction has been reported to occur with aniline, benzaldehyde and 8-quinolinol, yielding 7-α-anilinobenzyl-8-quinolinol (Pirrone, *Gazzetta*, 1940, **70**, 520; 1941, **71**, 320).



(A)

These products (A) of reaction are compounds of the chelating type and are of interest as possible analytical reagents and for possible amoebecidal activity. Easy manipulation of the reaction, coupled with the potential usefulness of the products, has led several workers (Phillips *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 4306; *J. Org. Chem.*, 1954, **19**, 907) to explore its possibilities further.

In this paper the work has been extended, and the products from a number of aromatic primary amines and substituted aromatic and aliphatic aldehydes with 8-quinolinol are reported. Simple and poly-substituted aldehydes and amines have been used to study the effect of different substituents on the course of the reaction.

The reaction was carried out with benzaldehyde, salicylaldehyde, crotonaldehyde, heptaldehyde, *m*-hydroxybenzaldehyde and 6-bromo-*m*-hydroxybenzaldehyde with the aromatic primary amines, *o*-and *p*-anisidines, 4-chloro-2-nitroaniline, *o*-, *m*- and *p*-chloroanilines, 1:3:4-xylidine, *p*-phenetidine, *m*-and *p*-nitroanilines and anthranilic acid.

Experimental

The preparation of the compounds was carried out according to the procedure recommended by Phillips *et al.* (*loc. cit.*). Equimolar (0.01 mole) proportions of the aldehyde and the amine were dissolved in sufficient (95%) ethanol to just dissolve the Schiff's base,

which separated out. To this 0.01 mole of 8-quinolinol was added, and the mixture stoppered and left to stand at room temperature for 100 days. The precipitated product was removed by filtration and recrystallised from ethanol. The insoluble products were purified by repeated washings with alcohol. Acetone and glacial acetic acid were found to be unsuitable for crystallisation.

The time required for the first sign of precipitation to occur was recorded in each case (Table II). Precipitation continued slowly for many days after this time. Refluxing was normally without any effect on the speed of reaction, but in one instance, (I), the formation of the compound was facilitated.

Products were not obtained in 100 days' time from benzaldehyde with *p*-anisidine, 4-chloro-2-nitroaniline and *p*-phenetidine. Using salicylaldehyde, heptaldehyde or crotonaldehyde with *p*-nitroaniline, *p*-phenetidine, 4-chloro-2-nitroaniline, *o*-chloraniline, 1 : 3:4-xylidine, *p*-anisidine and anthranilic acid, the desired products could not be obtained.

The compounds can be represented by the general structural formula (A) (*vide supra*).

TABLE I

Substituted 7-α-anilino-8-quinolinols.

No.	R_1.	R_2.	Formula.	M.P.	Yield.	% Nitrogen. Found.	Calc.
I	C_6H_5-	*p*-Cl−C_6H_4	$C_{22}H_{17}ON_2Cl$	114°	30%	6.9	7.77
II	C_6H_5-	*m*-$(CH_3)_2$−C_6H_3−	$C_{24}H_{22}ON_2$	140°	15	7.3	7.91
III	C_6H_5-	*o*-Cl−C_6H_4	$C_{22}H_{17}ON_2Cl$	128°	50	7.2	7.77
IV	C_6H_5-	*m*-NO_2−C_6H_4	$C_{22}H_{17}O_3N_3$	145°	85	10.7	11.30
V	*m*-OH.C_6H_4	*p*-NO_2−C_6H_4	$C_{22}H_{17}O_4N_3$	240°	90	10.2	10.85
VI	*m*-OH.C_6H_4	*o*-Cl−C_6H_4	$C_{22}H_{17}O_2N_2Cl$	102°	30	7.2	7.43
VII	*m*-OH.C_6H_4	*m*-Cl−C_6H_4	$C_{22}H_{17}O_4N_3$	158°	40	10.3	10.85
VIII	*m*-OH.C_6H_4	*o*-CH_3−C_6H_4	$C_{23}H_{20}O_2N_2$	172°	38	6.9	7.52
IX	6-Br-*m*-OH.C_6H_3	*p*-NO_2−C_6H_4	$C_{22}H_{16}O_4N_3Br$	193°	20	8.7	9.01
X	$CH_3(CH_2)_4CH_2-$	*p*-NO_2−C_6H_4	$C_{19}H_{25}O_3N_3$	103°	12	10.6	11.08
XI	*o*-OH.C_6H_4	4-Cl-2-NO_2−C_6H_3	$C_{22}H_{16}O_4N_3Cl$	175°	25	9.3	9.96

Spot Tests.—Colour reactions with concentrated sulphuric acid, concentrated nitric acid and 1% ferric chloride are spot tests for these products of reaction (Phillips *et al.*, *loc.cit.*). The first two of these, however, are not characteristic. Both were found to be positive in the case of the Schiff's base from salicylaldehyde and *p*-nitroaniline and only the 1% ferric chloride test responded negative. On the other hand, (VIII) reacted positive only to the ferric chloride test. Thus in the characterisation of these products, the ferric chloride test is the specific one, while the other two are secondary.

TABLE II

No.	Time for first sign of ppt.	Colour reaction with Conc. H_2SO_4.	Conc. HNO_3.	1% $FeCl_3$.
I	68 days	Red	Yellow	Green
II	45	,,	Yellow (persists)	,,
III	35	,,	Yellow	,,
IV	8	,,	,,	,,
V	1½	,,	,,	,,
VI	39	,,	,,	,,
VII	38	Dark brown	,,	,,
VIII	8	Yellow	,,	Green black
IX	22	Deep brown	,,	Green
X	45	Yellow	,,	,,
XI	65	Red	,,	,,

CONCLUSIONS

Compounds containing a nitro group were yellow while all others were tinged or colorless.

The study yielded the following further conclusions :

(1) The most active amine in all cases was found to be *para*-nitroaniline. Comparatively speaking, the order of reactivity of the nitroanilines is *para* > *meta* > *ortho*.

(2) The methoxy group in the *ortho*-position to the amino group disposes more favourably than that in the *para*-position, towards the speed of reaction.

(3) Benzaldehyde was found to be more reactive than its substituted derivatives.

(4) *m*-Hydroxybenzaldehyde gave products with a number of amines. Of the three substituted hydroxybenzaldehydes, *meta*-isomer was found to be the most reactive.

(5) In the case of 6-bromo-*m*-hydroxybenzaldehyde, the bromine in the *ortho*-position decreased the rate of reaction.

(6) In the cases studied, it has been observed that the effect of introducing substituents in the aldehyde part is to decrease the yield and rate of reaction (cf. benzaldehyde, *m*-hydroxybenzaldehyde and 6-bromo-*m*-hydroxybenzaldehyde with *p*-nitroaniline and 1:3:4-xylidine).

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SALICYLAMIDOXIME AS AN ANALYTICAL REAGENT. PART II. GRAVIMETRIC ESTIMATION OF COPPER AND NICKEL AND THEIR SEPARATION FROM OTHER METALS

By Debabrata Bandyopadhyay and Priyadaranjan Rây

The use of salicylamidoxime as a reagent for the gravimetric estimation of copper and nickel by weighing the precipitates of composition $M(C_7H_7O_2N_2)_2$, where M=Cu or Ni, after drying at 110°, is described. Copper can be effectively separated from mercury^{II}, lead, cadmium, zinc, manganese^{II} and cobalt^{II} by precipitating the copper with an excess of the amidoxime at a p_H of 4.0-4.5; while for the separation from iron^{III}, antimony^{III} and bismuth^{III}, the precipitation should be carried out in presence of sufficient tartaric acid at a p_H of 4.0-4.5. Nickel can similarly be separated from zinc quantitatively by precipitation with the reagent at a controlled p_H (7.0-7.5) in the presence of some ammonium chloride to prevent the precipitation of the latter element. Determinations of copper and nickel in mixed solutions have been carried out by precipitating copper in an acetate-buffer of p_H near about 4; in the filtrates nickel was precipitated by adding more of the reagent and then ammonia to adjust the p_H of the solution to 7.0-7.5.

The precipitation reactions of salicylamidoxime with metallic ions have been described in a previous communication (cf. Part I, this *issue*, 21). It has been stated there that copper and nickel are quantitatively precipitated from 0.001*M* solutions of the metals at p_H 3.9-6.5 and at 6.5-8.0 respectively for the two elements. These precipitates after drying at 110° have the composition given by $M(C_7H_7O_2N_2)_2$, where M=Cu or Ni. Furthermore, the p_H values of incipient precipitation of some metals in equivalent solutions by salicylamidoxime differ widely. From a consideration of all these facts salicylamidoxime might be expected to furnish suitable methods for the gravimetric determinations of copper and nickel as also for their separation from one another and from other metals. In this respect the amidoxime has several advantages over the aldoxime, which behaves analogously (cf. Welcher, "Organic Analytical Reagents", Vol. III, pp. 259-271, D. Van Nostrand Co., Inc., 1947). In fact, in contrast to salicylaldoxime, salicylamidoxime is rather stable, and consequently precipitations of metallic ions by this reagent can be carried out in hot solutions, and the precipitates can safely be washed with hot water, in which the reagent is fairly soluble. These are some of the factors that minimise entrainment of the precipitates with impurities. Moreover, the reagent is readily soluble in dilute acids and alkalies, and the acid solutions keep quite well, at least for several weeks at room temperature, in which it has been ordinarily used, although a solution in hot water is a good substitute. The reagent can be easily prepared in a pure state as described in the previous communication (*loc. cit.*). Actual determinations with varying amounts of copper (6 to 100 mg.) and of nickel (6 to 77 mg.) by precipitation with an excess of salicylamidoxime at a p_H of 4.0-4.5 for copper and 7.0-7.5 for nickel have yielded excellent results (cf. Tables I and VII respectively).

As the p_H limits for the precipitation of copper and nickel differ rather widely, a simple precipitation at a controlled p_H might be expected to effect their

separation. But actual experimental results showed that even at a p_H as low as 4 the copper precipitate, obtained in a mixture of copper and nickel, was sufficiently entrained with the latter. Precipitation in the presence of sufficient ammonium chloride also proved of little use in preventing the adsorption of nickel. This co-precipitation of an unusual type is possibly due to a similarity in the crystal structures of the compounds of the two metals in question.

Copper and nickel can, however, be effectively separated by precipitating the copper compound in an acetate-buffer medium of p_H about 4 (cf. Table VIII). This seems to indicate some specific influence of the acetate in preventing the co-precipitation of the nickel in this case. In the combined filtrate and washings nickel was determined by adding more reagent and adjusting the p_H with ammonia, as in the case of the individual nickel determination.

Copper has, however, been separated from zinc, cadmium, manganese^{II}, cobalt^{II}, lead and mercury^{II} by precipitation at a controlled p_H with the amidoxime (cf. Tables II-IV); but in the presence of mercury the addition of a sufficiently large excess of the reagent is essential for the complete precipitation of copper.

Interference by antimony^{III} and bismuth^{III} in copper determination can be prevented altogether by precipitating copper as usual, but in the presence of some tartaric acid as a masking agent. These results are shown in Table V. For the separation of copper from iron^{III}, the presence of tartaric acid is necessary as also of a large excess of the reagent (cf. Table VI).

Estimation of nickel can be carried out even in the presence of zinc by precipitating the nickel complex of the reagent in presence of sufficient ammonium chloride at a p_H of 7.0-7.5 (cf. Table IX); the latter prevents the precipitation of zinc.

EXPERIMENTAL

A pure sample of the reagent was prepared as described in Part I of this communication (*loc. cit.*).

Estimation of Copper

A stock solution of standard copper^{II} chloride was prepared from a known weight of metallic copper (G. R.) by dissolving it in nitric acid and evaporating the solution with hydrochloric acid. Its strength was further determined gravimetrically with salicylaldoxime.

A definite volume of the standard copper solution was just neutralised with pure ammonia and weakly acidified with hydrochloric acid and then diluted to about 100 c.c. with water and warmed on the water-bath. Copper was precipitated by adding an excess of the reagent (3.5-4.0 c.c. of the 1% solution in hot water or dilute hydrochloric acid for every 5 mg. of copper present in the solution) and adjusting the p_H of the solution to 4.0-4.5 (tested by B.D.H. indicator paper) by adding dilute alkali (KOH, NaOH or ammonia). The mixture was digested on the water-bath

for about 5-10 minutes in order to allow the precipitate to settle and then filtered through a sintered glass (Jena) Gooch crucible (No. 4). The precipitate was thoroughly washed with hot water dried at 110°, for at least one hour, in an air oven, and weighed. The factor for copper is 0.1740. The results are recorded in Table I.

TABLE I

Drying temp. = 110°.

Cu present.	Cu-compound.	Cu found.	Error (mg.).	Cu present.	Cu-compound.	Cu found.	Error (mg.).
0.00610 g.	0.03508 g.	0.00510 g.	±0.0	0.04629 g.	0.026604 g.	0.04629 g.	±0.0
0.01526	0 08775	0.01526	,,	0.05189	0.29802	0.05186	−0.03
0.02543	0.14595	0.02538	−0.05	0.06104	0.35100	0.06107	+0.03
0.03612	0.20775	0.03615	+0.03	0.07580	0.43579	0.07583	+0.03
				0.10276	0.59103	0.10283	+0.07

Separation of Copper from Cadmium and Zinc

From mixed solutions containing copper and the other metal, copper was precipitated as in the previous case. In the filtrates the other metals were determined gravimetrically as oxinates, after decomposing the excess of the amidoxime by fuming with nitric and sulphuric acids. The results are shown in Table II.

TABLE II

Metals present.	Cu-compound.	Metals found.	Error (mg.).	Metals present.	Cu-compound.	Metals found.	Error (mg.).
Cu, 0.05282 g.	0.30392 g.	0.05288 g	+0.06	Cu, 0 05282 g.	0.30342 g.	0.05279 g.	−0.03
Cd, 0 05428		0 05418	−0.10	Zn, 0.05102		0.05128	+0.08
Cu, 0.01098	0.06300	0 01096	−0.02	Cu, 0.01046	0.06001	0.01044	−0.02
Cd, 0.03225		...	...	Zn, 0.05120	...	..	...
Cu, 0.01203	0.06905	0.01201	−0.02	Cu, 0.01150	0.06594	0.01148	−0.02
Cd, 0.06450		...	...	Zn, 0.10291		0.10280	−0.11
Cu, 0 01150	0.06622	0.01152	+0.02	Cu, 0.10460	0.601?5	0.10462	+0.02
Cd, 0.09783		0.09777	−0 06	Zn, 0.01024		0.01030	+0.06
Cu, 0.09414	0.54070	0.09408	−0.06	Cu, 0.07845	0.45120	0.07850	+0.05
Cd. 0.01075		0.01077	+0.02	Zn, 0.01024		...	...
Cu, 0.06276	0.36005	0.06266	−0.10	Cu, 0.05492	0.31598	0.05498	+0.06
Cd, 0.01156		...	...	Zn 0.01126		...	...
Cu, 0.03243	0.18614	0.03239	−0.04				
Cd, 0.01236		...	...				

Separation of Copper from Cobalt, Manganese and Lead

In the case of separation from lead, mixed solutions containing copper nitrate and lead acetate were used as the absence of chloride and sulphate was essential.

The mixed solution containing copper and the other metal was neutralised with sodium carbonate, acidified with acetic acid and diluted to 150 c.c. with water. This was warmed on the water-bath for some time to expel the carbon dioxide, and the copper was precipitated as usual with the amidoxime at a p_H of 4.0-4.5. The precipitate was filtered, washed, dried and weighed as usual, while in the combined filtrate and washings the other metal was determined gravimetrically as the sulphate as usual after decomposing the organic matter by fuming with sulphuric and nitric acids. The results of some determinations are shown in Table III.

TABLE III

Metals present.	Cu-compound.	Metals found.	Error (mg.).	Metals present.	Cu-compound.	Metals found.	Error (mg.).
Cu, 0.05492 g.	0.31590 g.	0.05495 g.	+0.03	Cu, 0.05230 g.	0.30032 g.	0.05225 g.	−0.05
Co, 0.05788		...	...	Mn, 0.00931		0.00935	+0.04
Cu, 0.05544	0.31868	0.05546	+0.02	Cu, 0.01307	0.07527	0.01309	+0.02
Co, 0.01158		0.01160	+0.02	Mn, 0.05819		...	...
Cu, 0.01150	0.06619	0.01152	+0.02	Cu, 0.05561	0.31960	0.05560	−0.01
Co, 0.06367		...	...	Pb, 0.05228		...	...
Cu, 0.05230	0.30022	0.05223	−0.07	Cu, 0.01145	0.06574	0.01144	−0.01
Mn, 0.04888		...	...	Pb, 0.05228		...	...
				Cu, 0.05496	0.31583	0.05494	−0.02
				Pb, 0.01098		0.01095	−0.03

Separation of Copper from Mercury

This can be effected by precipitating the copper from mixed solutions containing copper^{II} chloride and mercury^{II} chloride at a p_H of 4.0-4.5, but a relatively large excess of the amidoxime, determined by the amount of mercury present, is required to effect complete precipitation of copper (cf. Table IV).

The mixed solution containing copper^{II} and mercury^{II} chlorides was neutralised with caustic soda, acidified with HCl, diluted to 200 c.c. with water, warmed and treated with an excess of the reagent solution, p_H adjusted to 4.0-4.5, and the copper precipitate was worked up as usual. In the filtrate mercury was determined gravimetrically as the sulphide. The results are shown in Table IV.

TABLE IV

Metals present.	Volume of 1% reagent soln.	Cu-compound.	Metals found.	Error.
Cu, 0.05256 g.	60 c c.	0.30180 g.	0.05250 g.	−0.06 mg.
Hg, 0.04830		...	...	...
Cu, 0.06302	50	0.36237	0.06305	+0 03
Hg, 0 01449			0.01451	+0.02
Cu, 0.01046	10	0.05420	0.00943	−1.03
Hg, 0.04830			...	...
Cu, 0 01046	30	0.06020	0.01047	+0.01
Hg, 0.04830			...	...

Separation of Copper from Antimony and Bismuth

To the mixed solution containing copper^{II} chloride and antimony^{III} ch'oride or copper^{II} nitrate and bismuth^{III} nitrate, as the case may be, sufficient free mineral acid was added to afford a clear solution. This was treated with about 2.5 g. of Rochelle salt and then with sodium carbonate solution till a light blue colour just appeared. The solution was then acidified carefully by adding the requisite mineral acid to bring its p_H between 4 and 5. This was then diluted to about 200 c.c. with water, warmed on the water-bath, and copper precipitated by adding an excess of 1% aqueous solution of the amidoxime and then adjusting the p_H, if required, to 4.0-4.5 by adding a dilute solution of caustic potash. The copper precipitate was filtered, washed, dried and weighed as usual. In the filtrate antimony was determined volumetrically by the bromate method, and bismuth determined gravimetrically as the oxide (Bi_2O_3), after precipitation with ammonium carbonate ; all organic matter was previously decomposed by fuming with sulphuric and nitric acids. The results of a number of determinations are recorded in Table V. That tartaric acid did not interfere with the determination of copper is shown by the first two results in the table.

TABLE V

Metals present.	Cu-compound.	Metals found.	Error.
Cu, 0.01308 g.	0.07542 g.	0.01312 g.	+0.04 mg.
Cu, 0.10460	0.60180	0.10470	+0.10
Cu, 0.04184	0.23998	0.04176	−0.08
Sb, 0.02394		...	...
Cu, 0.05282	0.30382	0.05284	+0.02
Sb, 0.00599		...	...
Cu, 0.01046	0.05995	0 01043	−0 03
Sb, 0.02993		0.02981	−0.12
Cu, 0.04253	0.24492	0.04261	+0.08
Bi, 0.04889		0.04898	+0.09
Cu, 0.06543	0.37620	0.06545	+0.02
Bi, 0.01528		...	...
Cu, 0.01309	0.07544	0.01313	+0.04
Bi, 0.07334		...	...

Separation of Copper from Iron

Copper has been separated from iron^{III} by precipitating the former in presence of tartaric acid at a p_H of 4.0-4.5 by using a large excess of the reagent. About 3.5-4.0 c.c. of 1% solution of the reagent for each 5 mg. of copper and in addition 8-9 c.c. of the same for each 5 mg. of iron present have been found necessary for complete separation.

The mixed solution containing copper^{II} and iron^{III} chlorides and sufficient HCl was treated with 3 g. of Rochelle salt; this was diluted to 150 c.c. and warmed on the water-bath. The hot solution was treated with the requisite quantity of the reagent solution, prepared in 0.1*N* hydrochloric acid, and the p_H adjusted thereafter to 4.0-4.5 by adding dilute caustic potash solution. The copper precipitate was worked up as usual, and in the filtrate iron was determined gravimetrically as Fe_2O_3, after decomposing the organic matter. The results of some of the determinations are shown in Table VI.

TABLE VI

Metals present.	Volume of 1% reagent soln.	Cu-compound.	Metals found.	Error.
Cu, 0.05230 g.	40 c.c	0.29741 g.	0 05168 g.	−0 062 mg.
Fe, 0.01082			...	...
Cu, 0.01046	10	0.05875	0.01022	−0.24
Fe, 0.00541			...	...
Cu, 0.05282	40	0 30385	0.05286	+0.04
Fe, 0.00054			...	...
Cu, 0.06276	150	0.36101	0.06281	+0 05
Fe, 0.06042			...	...
Cu, 0.03138	80	0.18040	0.03138	±0.0
Fe, 0.03021			0.03020	−0.01
Cu, 0.01046	60	0.06017	0.01046	±0.0
Fe, 0.03021			0.03013	−0.08

Estimation of Nickel

A stock solution of nickel chloride was prepared and its strength was determined gravimetrically as nickel-dimethylglyoxime. A known volume of the nickel solution was diluted to about 100 c.c. by adding water, warmed on the water-bath, added an excess of the reagent solution (about 4 c.c. of the 1% solution, in 0.1*N*-HCl or hot water, for every 5 mg. of the nickel present) and dilute ammonia was then gradually added till the p_H of the solution came within the range of 7.0-7.5 (tested by B.D.H. indicator paper). This was then digested on the water-bath till the precipitate settled down (about 10-15 minutes required). The precipitate was then filtered off on a No. 4 sintered glass (Jena) Gooch crucible, washed thoroughly with hot water of p_H near about 7 (adjusted by adding a few drops of dilute ammonia) and then dried at 110° for at least one hour and weighed. The factor for nickel is 0.1628 Results are recorded in Table VII.

TABLE VII

Drying temp. = 110°.

Ni present.	Ni-compound.	Ni found.	Error.
0.00662 g.	0.04064 g.	0.00662 g.	±0.0 mg.
0.02597	0.15958	0.02599	+0.02
0.05143	0.31557	0.05138	−0.05
0.06212	0.31891	0.06218	+0.06
0.07740	0.47569	0.07744	+0.04

Estimation of Copper and Nickel when present together

The mixed solution containing copper and nickel was neutralised with dilute ammonia till a turbidity just appeared. To this were added 6 c.c. of 6*N* acetic acid and 10 c.c. of a 10% solution of sodium acetate. The mixture was then diluted to 100 c.c. with water and warmed on the water-bath; copper was then precipitated in hot solution by adding 4.0-4.5 c.c. of an 1% solution of salicylamidoxime in hot water for every 5 mg. of copper present. This was then digested on the water-bath for about 10 minutes and then filtered hot through a No. 4 sintered glass (Jena) Gooch crucible. The precipitate was washed thoroughly with hot water, then dried at 110° for one hour and weighed. In the combined filtrate and washings nickel was precipitated by adding more of the reagent (about 4 c.c. of the 1% solution for every 5 mg. of nickel present) and then adjusting the p_H to 7.0-7.5 with ammonia. The results of some of the determinations are recorded in Table VIII.

TABLE VIII

Metals present.	*p_H.	Wt. of compounds.	Metals found.	Error.
Cu, 0.01569 g.	3.92	0.09001 g.	0.01566 g.	−0.03 mg.
Ni, 0.01527		0.09386	0.01529	+0.02
Cu, 0.04759	3.98	0.27301	0.04750	−0.09
Ni, 0.01578		0.09712	0.01581	+0.03
Cu, 0.09336	3.88	0.53610	0.09328	−0.08
Ni, 0.01604		0.09871	0.01607	+0.03
Cu, 0.01674	4.08	0.09619	0.01673	−0.01
Ni, 0.04837		0.29657	0.04829	−0.08
Cu, 0.01569	3.98	0.09001	0.01566	−0.03
Ni, 0.09267		0.56956	0.09273	+0.06
Cu, 0.05308	3.94	0.30499	0.05307	−0.01
Ni, 0.05423		0.33282	0.05418	−0.05

* The p_H values refer to the filtrate only.

Separation of Nickel from Zinc

An excess of ammonium chloride has been found to prevent the precipitation of zinc.

The mixed solution containing nickel and zinc was treated with about 4 g. of ammonium chloride, diluted to 200 c.c. with water and heated on the water-bath. To the warm solution was added an excess of the reagent (about 4.0-4.5 c.c. of the 1% solution of salicylamidoxime, in 0.1*N*-HCl for every 5 mg. of nickel present) and nickel was precipitated by adding dilute ammonia dropwise till the p_H of the solution rose to 7.0-7.5 (tested by B.D.H. indicator paper). The mixture was digested on the water-bath for a few minutes and then the precipitate was filtered, washed, dried and weighed as usual.

In the combined filtrate and washings, zinc was estimated gravimetrically as the oxinate, after decomposing the organic matter. The results of some of the determinations are shown in Table IX. The first two results in the table indicate that ammonium chloride does not interfere with the determination of nickel.

TABLE IX

Metals present.	Ni-compound.	Metals found.	Error.
Ni, 0.01399 g. Zn, nil	0.08618 g.	0.01403 g.	+0.04 mg.
Ni, 0.12562 Zn, nil	0.77276	0.12581	+0.19
Ni, 0.10184 Zn, 0.01024	0.62580	0.10190 ...	+0.06 ...
Ni, 0.01069 Zn, 0.05120	0.06580	0.01071 ...	+0.02 ...
Ni, 0 01247 Zn, 0.1024c	0.07623	0.01242 ...	−0.05 ...
Ni, 0.06219 Zn, 0.01024	0.38231	0.06224 0.01030	+0.05 +0.06
Ni, 0.06281 Zn, 0.05120	0.38594	0.06284 0.05128	+0.05 +0.08

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SORPTION OF WATER VAPOUR BY POWDERED *CICER ARIETINUM*. HEAT OF SORPTION

By B. P. Gyani

The sorption of water and toluene vapours on gram powder (*Cicer arietinum*) has been studied with a view to ascertaining the fate of the sorbed vapour. Three samples of powder (alkali-washed, toluene-washed and untreated) have been used. The isosteric heats of sorption have been determined. It appears that at least the first lots of water vapour taken up correspond to persorption rather than capillary or multi-layer condensation. Alkali-washed and toluene-washed samples show similar enhancement of sorption over the untreated powder. The heat of sorption decreases sharply from over 20, 000 cal./mole at low values of sorption to about the latent heat of condensation of high values.

Makower ("Analytical Methods in Food Chemistry", American Chemical Society, 1950, p. 37) points out that "the moisture determination is perhaps one of the most widely used analytical measurements in processing and testing food products..... moisture content is frequently an index of stability and quality of food". However, he discusses in detail that moisture determination in vegetables and fruits is a difficult matter. The difficulties are much lessened with corn and perhaps other grains. Sair and Fetzer (*Cereal Chem.*, 1942, **19**, 633) found that corn might be heated to 110° in contact with boiling toluene without decomposition, while vegetables started decomposing around 70°.

Makower doubts the utility of using moisture content of the whole food as a critical variable, because the moisture is not uniformly distributed among the various constituents. Thus, for example, the moisture content may be a sum of the constituent starch, protein, sugar and cellulose. Each of these is determined by the relative humidity and is described by an isotherm for the component. The overall moisture is therefore of little significance since the water content of the most sensitive component will determine deterioration. Hence, Makower and Miss Myers (*Proc. Inst. Food Technol.*, 1943, 156) have suggested the equilibrium pressure of water vapour as an index of moisture. They, however, remark that "At the present time very few vapour pressure data are available for foods".

It is partly to provide data of this kind as well as make an attempt to ascertain how the water exists in the grain that the present work has been undertaken. It might appear at first sight that any theoretical approach from the point of view of sorption will be futile considering the chemically heterogeneous character of the material. However, it is difficult to think of a solid adsorbent which is chemically homogeneous (not excluding adsorbent silica or alumina). A chemically homogeneous solid may yet be physically inhomogeneous, as has been discussed by the author in two earlier papers (*J. Phys. Chem.*, 1945, **49**, 442 ; *J. Phys. Coll. Chem.*, 1949, **53**, 1091). The capillary condensation theory in any case completely ignores the chemical nature of the adsorbing material (as long as it is wetted by water). It appears that for most theoretical purposes gram powder is as good an adsorbent as any other powdered solid.

Cicer arietinum is a common Indian gram with a large protein content, albuminoids 21.7%, water 11.5%, starch 59%, oil 4.2%, fibre 1%, ash 2.6% including phosphoric acid 1.1%, for husked seeds (Church, "Food Grains of India," cited by Watt, "Economic Products of India," Vol. 2, p. 210, Calcutta, 1889). The composition is, of course, variable as will appear from another typical analysis: moisture 9.8%, protein 17.1%, fats (ether extract) 5.3%, minerals 2.7%, fibre 3.9%, carbohydrates 61.2%, calcium 0.19% and phosphorus 0.24% for the whole grain ("Wealth of India", Vol. 2, p. 154, New Delhi, 1950).

Experimental

The grains were split to remove the skin and powdered to 40-60 mesh. One portion was refluxed with dilute sodium hydroxide, washed thoroughly with distilled water and dried. Another portion was refluxed with excess of toluene and dried. A third portion was not subjected to any washing. It was evacuated at 55° before taking sorption measurements. It was then evacuated at 100° before another run. An excess of water was then added to the powder, the containing bulb maintained in boiling water for half an hour, and the sample then evacuated at 100° for fresh runs. Finally, it was evacuated at 250° for the last set of measurements. The sorption apparatus used has been previously described (this *Journal*, 1949, **26**, 308). The sorption bulb was maintained at constant temperatures with the help of a Dewar flask containing suitable bath meterials.

Table I

Sorption on alkali-washed gram powder.

x/m = mg. water sorbed per g. of powder. p = pressure in mm. oil.
(1 mm oil = 0.0714 mm. mercury).

	Temp. = 0°. Desorption.						Temp. = 0°. Adsorption.			
p	61	60	58	49	32	10	16	25	45	61
x/m	488	387	302	210	164	100	72	99	169	279

	Temp. = 10°. Desorption.									
p	124	121	118	100	79	56	40	29	19	3
x/m	403	350	334	201	166	133	111	97	81	52

	Temp. = 20°. Desorption.														
p	232	229	221	197	165	146	128	102	80	73	55	44	32	22	10
x/m	322	274	238	195	171	152	139	121	108	103	85	79	71	59	44

	Temp. = 30°. Desorption.								Temp. = 40°. Desorption.								
p	252	197	158	115	89	64	39	34	16	278	228	200	165	139	112	86	76	43	9
x/m	139	118	102	82	71	66	54	48	31	87	80	75	68	63	56	50	43	36	19

The sorption data for water and toluene are shown in Tables I-IV. Some of the isotherms are shown in Fig. 1 in which x/m = mg. water vapour (or toluene) sorbed per g. of powder is plotted against the equilibrium pressure in mm. oil (1 mm. oil = 0.0714 mm. mercury). As far as one can see all the isotherms belong to Type II, (Brunauer, "Adsorption of Gases and Vapors", p. 150, Princeton University Press, 1943), excepting the water isotherm for the powder evacuated at 250°. It appears from the sorption data that sorption hysteresis exists in all cases of water sorption excepting the last mentioned. The hysteresis commences at the lowest pressures. This unusual observation may not have been possible without the sensitive oil manometer.

TABLE II

Sorption on toluene-washed gram powder.

Temp. = 0°. Desorption.

p	62	62	58	45	32	9
x/m	337	317	273	183	137	79

Temp. = 0°. Adsorption.

p	25	35	44	62
x/m	110	128	154	370

Temp. = 10°. Desorption.

p	130	127	116	86	52	19
x/m	495	417	296	168	109	74

Temp. = 20°. Desorption.

p	232	210	162	96	51	12
x/m	308	243	143	105	81	53

Temp. = 30°. Desorption.

p	276	250	204	180	115	77	45	21	3
x/m	135	126	111	101	87	68	57	50	29

Temp. = 30°. Adsorption.

p	14	60	101	153	194	208
x/m	33	52	64	77	87	95

Temp. = 40°. Desorption.

p	287	282	235	203	151	125	103	80	77	67	18	6	small
x/m	91	90	82	78	70	66	62	57	54	51	30	20	6

TABLE III

Sorption on untreated gram powder.

Temp. = 0°. Powder evacuated at 55°-60° and flushed several times.

Desorption.

p	62	59	57	53	46	41	35	22	10	small
x/m	178	160	147	125	102	89	77	64	47	26

Temp. = 35°. Desorption, on the same sample.

p	234	218	190	173	147	126	102	88	67	51	34
x/m	41	39	37	35	33	32	28	26	22	20	15

Temp. = 0°. Powder moistened with water and heated at 100° for ½ hour, then evacuated at 100°.

Desorption.

p	62	60	58	54	37	15
x/m	256	219	165	119	81	55

Temp. = 0°. Powder evacuated for half an hour at 250°-270°. Desorption.

p	62	39	31	26	21	11
x/m	38	37	36	34	32	24

TABLE IV

Sorption of toluene on gram powder (desorption).

Temp. = 0°.

	Toluene-washed-powder.				Alkali-washed-powder.			
p	96	41	15	small	92	87	14	3
x/m	22	6	5	3.2	44	8	2.2	1.8

TABLE V

Heats of desorption from isosteres.

Q (cal./mole) corresponding to amounts sorbed at 20°.

	Water on alkali-treated gram.				Water on untreated gram (Table III, first two runs)	
x/m	40	50	80	100	30	40
Q	20150	16030	13930	11310	17640	14170

Water on toluene-washed gram.

x/m	40	60	80	100	120	140	180	220
Q	23640	18020	14090	12940	11340	10570	10100	10020

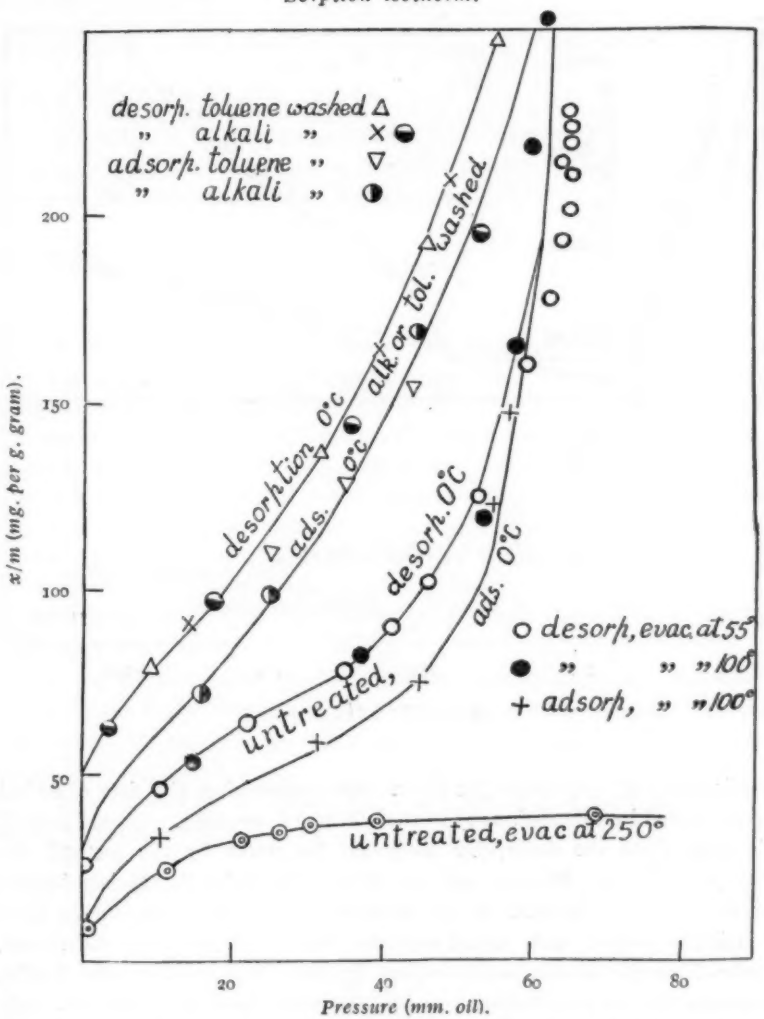
The amounts of sorption in these tables may be converted into c. c./g. powder. It would then appear that a far smaller volume of toluene is taken up than water under similar conditions. Even at saturation pressure, the volume of toluene sorbed is much less than that of water. Clearly therefore the principal process involved is not capillary condensation.

DISCUSSION

Washing with alkali or toluene considerably enhances sorption for water. It is interesting that the increase is almost the same in each case. As a matter of fact the sorptions for the two samples are almost coincident at any temperature. However, in the sorption of toluene, the toluene-treated sample shows a larger capacity (Table IV). Solid circles on the desorption isotherm of untreated gram in Fig. 1 correspond to the sample which has been boiled in contact with water before evacuation. Boiling is likely to produce changes in the gram (e.g. bursting of cells), but strangely enough, the sorptive properties are not affected. Table III shows that evacuation at 55°-60° is not enough to remove all the water from the powder. The apparent x/m values are therefore smaller than those for the same sample evacuated at 100°.

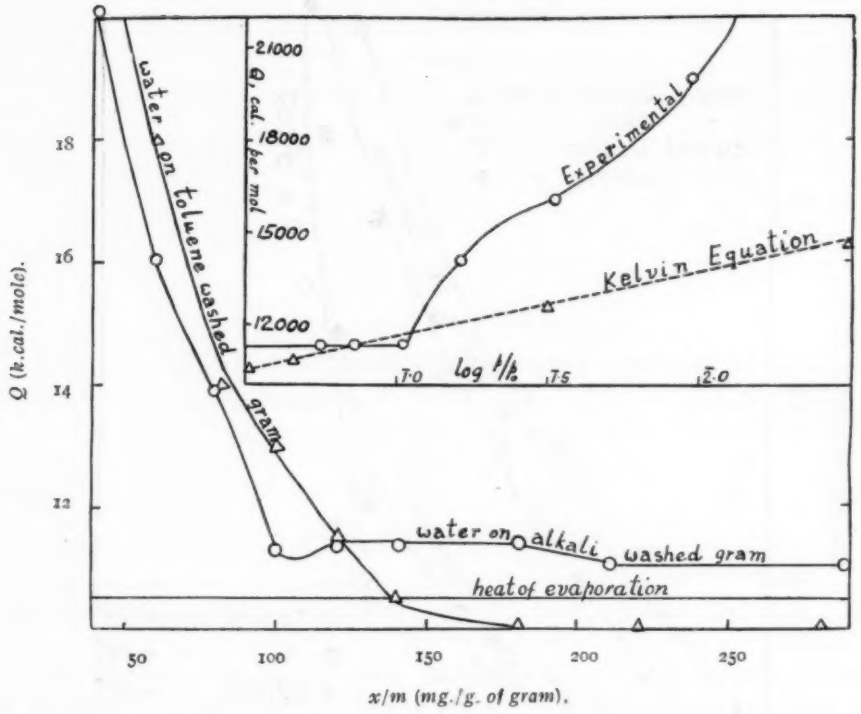
FIG. 1

Sorption isotherm.



Most of these curious observations are easily understood if we consider that the main process concerned in these sorptions is a deep and highly disperse penetration of the sorbed molecules in the material of the adsorbent, a process akin to persorption rather than capillary or multi-layer condensation. This would explain the enhancement of sorption on washing with toluene or alkali (removal of fatty matter and opening up structures for penetration of water molecules), the much smaller sorption of toluene (hindrance to penetration due to large size of toluene molecules), and indifference towards boiling as far as water sorption is concerned, since the cell wall is already freely pervious to water molecules.

FIG. 2 FIG. 3



Isosteric Heats of Sorption.—The above view concerning the fate of sorbed water is further supported by calculations of isosteric heats of sorption. These heats (Q) have been calculated from the desorption isotherms for water by the method discussed before (this *Journal*, 1949, **26**, 345) and are shown in Table V. Q has been plotted against x/m in Fig. 2. In spite of the apparent similarity of the curves for the two samples (toluene-washed and alkali-washed), the Q values show differences. The toluene-treated sample shows larger values initially, but smaller ones finally. The curve becomes flat at x/m=about 100 for the alkali washed gram, but only at a higher value, about 140, for the toluene washed-sample. In both cases Q tends to attain the value of latent heat of evaporation of water at high x/m. The widely variable Q is fundamentally opposed to the possibilities of the sorbed water being present as capillary condensed or multi-layer condensed water. The latter presumes a constant value for Q. The former does require a variation of Q, but of a smaller order. Proceeding from the Kelvin equation

$$RT \ln \frac{p}{p_o} = - \frac{\sigma V}{r} \quad \ldots \quad \ldots \quad (i)$$

one can obtain the equation

$$Q = L + RT \ln \frac{p_o}{p} \left(1 - \frac{d\ln\sigma}{d\ln T}\right) \quad \ldots \quad \ldots \quad (ii)$$

where L = molar latent heat of evaporation, V = molar volume, r = radius of meniscus of the capillary condensed liquid and σ = surface tension. Taking σ = 72.66 at 292° K and 72.73 at 294° K, equation (*ii*) may be written as

$$Q = L + 2.303 \times 1.59 \log \frac{p_o}{p} \quad \ldots \quad \ldots \quad (iii)$$

For the simple capillary condensation one should expect a straight line graph between Q and $\log p_o/p$ (p_o = saturation pressure and p = equilibrium pressure at the given temperature). The graph corresponding to equation (*iii*) and the experimental graph are shown in Fig. 3 (inset in Fig. 2). The two graphs are widely separated and the experimentally obtained Q values are generally much larger than those from (*iii*). It is clear that the adsorbent material is exerting a more specific effect on the sorbed water. It can hardly do so without coming in intimate contact with most of the sorbed water molecules, such as takes place in persorption. The structure of the material responsible for persorption is broken down perhaps near 250°, when the sorption falls down steeply, and the isotherm becomes indicative of simple surface adsorption (Type I isotherm).

We have stated above that gram ordinarily contains about 10% moisture (x/m = 100). On the basis of the above study it appears reasonable to conclude that practically all of this water is intracellular. Dry gram contains little water condensed in the intercellular capillary spaces, if any.

The author thanks Dr. B. Narayana, Vice Chancellor of the Patna University, for his constant encouragement.

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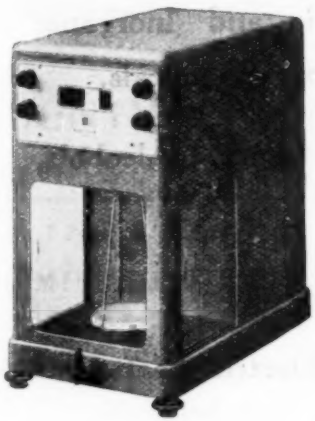

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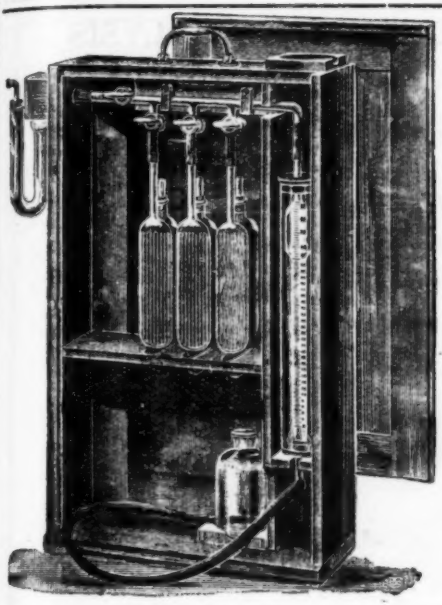

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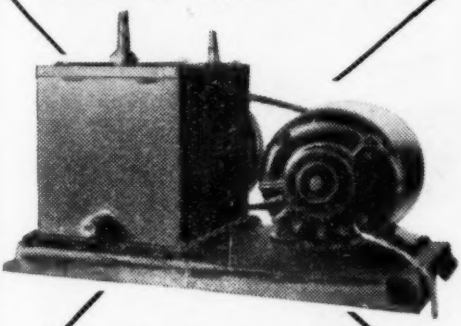

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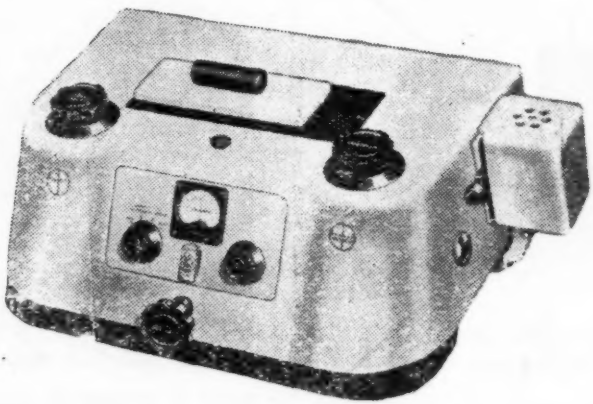

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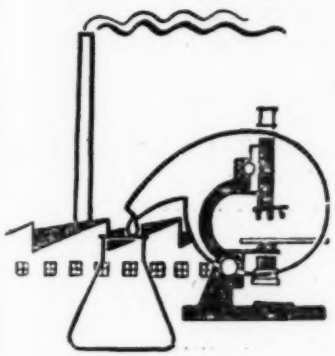

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